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Hydrothermal Liquefaction of Municipal Sludge and Biosolids

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Hydrothermal Liquefaction of Municipal Sludge and Biosolids

by

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Thesis

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Dedication

Dedicated to my sister Jane.

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I'd like to thank Cody Bond for his helpful collaboration, assistance with conducting experiments, and hard work to help me avoid a few minor crises. Thanks to Jenny Kondo for helping me avoid a few more. Thank you also to Dan Campell, Dan Pinero and Luis Galindo for making the laboratory an enjoyable workplace. I'd like to thank my advisor, Dr. Halil Berberoglu, for his insight and feedback that helped shape this thesis.

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Abstract

Hydrothermal Liquefaction of Municipal Sludge and Biosolids

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The conversion of municipal sludge and biosolids into bio-oil via hydrothermal liquefaction (HTL) can simultaneously provide a replacement to non-renewable crude oil while dealing with waste disposal issues. Hydrothermal liquefaction takes advantage of liquid water's interesting properties at high temperatures near the critical point, which facilitate the break down and reformation of biomass into a more energy dense bio-oil.

Several laboratory-scale batch HTL experiments have been conducted with algae, woody biomass and livestock manure, but few have considered municipal sludge or biosolids. Suzuki et al. (1988) and Vardon et al. (2011) conducted studies on the HTL of sludge and biosolids, however neither study explored the effect of processing conditions [1,2]. This thesis presents a study that explored how bio-oil composition and yield were affected by residence time, heating rate, initial biomass solids percentage and initial biomass composition. The highest quality bio-oil had a higher heating value (HHV) of 31.46±0.37 MJ/kg with a conversion yield of 39.42±1.4%. The HHV of the bio-oil was

increased when the initial biomass had a higher solids concentration or higher HHV. The conversion yield was larger at lower solids percentages and at a heating rate of 270˚C/min.

Furthermore, very few continuous HTL systems have been developed even though they may be the most viable option for scaling up. This thesis also presents the design and construction of a continuous HTL system for the processing of municipal sludge and biosolids.

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Chapter 1: Introduction

1.1 MOTIVATION

With recent nationwide focus on replacing fossil fuels with domestic renewables due to environmental and national security concerns, the hydrothermal liquefaction (HTL) of biomass has recently earned significant interest. Hydrothermal liquefaction is the process of heating and pressurizing an aqueous biomass slurry to 200-375˚C and 15-22 MPa (2200-3200 psi) in order to convert the biomass into an energy dense bio-oil phase. The byproducts are an aqueous phase, a solid charred phase and a gas phase. The process utilizes changes in water's solvation power, degree of hydrogen bonding, dielectric constant and ion product which occur as liquid water nears its critical point temperature [3]. These altered properties cause a breakdown of the input biomass slurry and reformation into the resulting bio-oil [3]. This oil has higher portions of hydrogen and carbon than the initial feedstock, giving it a heating value that can be nearly as high as traditional crude oil. The bio-oil may be directly used in some boiler applications or hydrotreated before being sent to oil refineries. The relative ease at which this oil could be incorporated into existing infrastructure makes HTL a viable method to produce a replacement fuel for the marine, land and aviation transportation sectors, which are not easily electrified. HTL, as opposed to pyrolysis or gasification, is an efficient conversion pathway for several types of biomass because it does not require the energy intensive step of drying out the biomass.

Several types of biomass have been successfully converted into bio-oil, including algae, trash, sludge, animal manure, residues from food processing, and woody biomass. The composition and yield of the resulting bio-oil depends greatly on the type of biomass input as well as the process conditions. The use of municipal sludge or biosolids as an HTL feedstock is of particular interest because it may simultaneously resolve issues with costly

sludge disposal as the harsh processing conditions of HTL are sufficient to sterilize the products of any biological pathogens [3]. Currently, the sludge must be subjected to expensive processes before it can be landfilled or used as fertilizer [4].

Current experimental HTL research focuses of increasing bio-oil yield and creating a bio-oil product that is more similar to traditional crude oil. In general, HTL bio-oil has a higher heteroatom content than crude oil, which causes negative effects including instability, a lower heating value and the potential to corrode processing equipment [5,6]. Several groups have experimented with using different feedstocks and process conditions to influence the yield and composition of the bio-oil, but before this thesis, research on the HTL of municipal sludge and biosolids had been very limited. Only two groups had processed municipal sludge and biosolids in batch reactors, and no group had created a continuous system to do so. The two groups that had performed batch HTL used consistent processing conditions and focused on the differences in bio-oil yield and composition caused by changing the feedstock type [1,2].

The goal of this thesis was to lay the groundwork for a full-scale HTL system to be built at the Hornsby Bend Biosolids Management Plant. In order for sludge and biosolids to be used in a full-scale HTL system, the feedstock and processing conditions needed to be optimized, and a small-scale continuous system was needed to demonstrate proof-of-concept. In this thesis, several batch experiments were conducted to determine how the heating rate, residence time, feedstock solids percentage and feedstock type affected the bio-oil yield and composition, specifically for samples from the Hornsby Bend Biosolids Management Plant. This research was a necessary step in working towards a full-scale HTL system at Hornsby Bend and was also beneficial to the HTL community in that it provided insights concerning the effect of processing conditions. Additionally, a laboratory scale continuous HTL system was constructed to demonstrate the processing of th sludge and

biosolids. The design of this system provided a template for designing the scaled-up system, and the successes and pitfalls in system construction will provide useful knowledge for scaled-up construction.

1.2 Organization of Thesis

Chapter 2 presents the current state of knowledge in the field. It first introduces the current procedures for processing sludge and describes how HTL may improve sludge management. Next, the issues due to dissimilarities between traditional petroleum and bio-oil are discussed. Finally, the relevant literature concerning batch and continuous HTL is discussed. Chapter 3 reports a batch reactor study for assessing the effects of residence time, heating rate, feedstock solids concentration and feedstock type on the bio-oil conversion yield and composition. Finally, Chapter 4 presents the engineering design of a continuous HTL system capable of converting sludge and biosolids to bio-oil at a slurry flow rate of 5-20 mL/min.

Chapter 2: Current State of Knowledge

2.1 Municipal Sludge and Biosolids Background

The management of sewage sludge is a growing issue around the world. The U.S. Environmental Protection Agency (EPA) estimates that the U.S. alone currently produces over 8 million dry tons of biosolids each year [4]. The level of pathogens in sludge is unsuitable for human contact, so it must be processed and/or disposed of in more complex and expensive methods than normal waste products. Approximately 40% is disposed of using expensive, non-beneficial methods such as incineration and landfilling [4]. However, the predominant method of dealing with sludge by anaerobically digesting it to produce biosolids which can be used for land applications [4]. The EPA defines sludge as residuals from wastewater processing while biosolids are 'the nutrient-rich organic materials resulting from treatment and processing of [these] wastewater residuals' [4].

Converting sludge into biosolids is a desirable pathway because it is more sustainable than landfilling and less energy intensive than burning, but the process still has substantial capital and operating costs [7]. Furthermore, once the sludge is converted, the biosolids must often be transported long distances for land application, which requires increased energy use and cost [7]. The literature shows that sludge and biosolids, as well as farm-generated manure, can be used as a viable feedstock for HTL [1,2]. There is also evidence that HTL mitigates the environmental impacts of sludge and biosolids by sterilizing it and removing almost all heavy metals [3,8]. Consequentially, the HTL process has the potential to reduce costs associated with anaerobic digestion and/or the transportation of biosolids while simultaneously producing bio-oil.

2.2 HTL BACKGROUND

Hydrothermal liquefaction has been considered as means for replacing traditional petroleum fuel for several decades. An NREL review of HTL by Jay Stevens reports that introductory research into HTL was initiated in response to high demand and fluctuating prices of petroleum in the 1970s [9]. The first significant work was done by the Pittsburgh Energy Research Center (PERC) starting in the early 1970s. PERC used woody biomass in an oil-based slurry with a sodium carbonate catalyst. After successful testing with a bench-scale batch process, the system was scaled up and converted to a continuous process at a demonstration plan in Albany, Oregon. Shortly thereafter, Lawrence Berkeley National Laboratory (LBNL) introduced a pretreatment of the wood, which addressed issues of undissolved solids and medium viscosity and allowed aqueous, rather than oil-based, slurry to be used. LBNL developed a bench-scale continuous HTL system and then also began working at the demonstration plant in Albany. The plant successfully produced 35 barrels of bio-oil, and in 1981, the plant produced 5000 kg of bio-oil during a 572 hour test run. The plant was then shut down and sold, having demonstrated that HTL could generate substantial bio-oil. From the mid-1980s until the 2000s, progress in HTL was mostly halted due to a decrease and stabilization in petroleum prices. [9]

With energy concerns growing again in the early 2000s, several groups began to use small batch reactors to test a range of HTL processing conditions and to more thoroughly analyze their effects on product yield and composition. Several types of biomass feedstocks have been tested with different solids contents and at several different pressures, temperatures, heating rates and residence times. Few of these studies, however, have used a sludge or biosolids feedstock. Suzuki et al. (1988) conducted batch experiments with several types of sludge, biosolids and mixed feedstocks and varied the catalyst loading [1]. Vardon et al. completed one experiment with biosolids and compared

it to experiments with algae and animal manure [2]. Neither of these studies explored the effect of process conditions.

In the 2010s, continuous HTL systems began to reemerge at both a bench- and pilot-scale. Pacific Northwest National Laboratory (PNNL) and the University of Sydney published papers that detailed bench-scale continuous systems used to process algal feedstock [10,11]. Companies such as Sapphire Energy, ThermoEnergy, Algenol (USA), SCF Technologies, Steeper Energy (Denmark), and Muradel (Australia) may also have developed continuous or semi-continuous systems, but their work is proprietary. There have been no continuous HTL systems used to process sludge or biosolids.

2.3 Bio-Oil Characterization

The intended purpose of HTL bio-oil is to provide a drop-in replacement for petroleum in areas such as air and ground transportation. Therefore, it important to understand the characteristics of petroleum as a point of comparison for bio-oil. In his *Handbook of Petroleum Analysis*, Speight defines petroleum as any hydrocarbon-rich fluid found in subterranean reserves [6]. The properties of petroleum vary considerably depending on its location of origin, and as a result, petroleum is very difficult to classify and analyze with a consistent methodology. Petroleum analysis can be different based on the petroleum's origin or desired end use, among other factors. Analysis continues to change significantly over time as testing technologies become more advanced. [6]

Speight indicates that the value of a given crude oil depends on how easily a refiner can use it to obtain a product that meets current market demand. The refiner is not ultimately concerned with the exact chemical structure of the petroleum, but the oil quality and difficulties in handling, refining and transporting it. The most important bulk properties in distinguishing between different crude oils are the boiling point distribution, density,

viscosity, water content and sulfur content. Sulfur is often considered the most important of the heteroatoms by refiners, however high levels of nitrogen, oxygen and trace metals can also cause problems as process units can see huge volumes of petroleum per day. The composition of petroleum is normally 83-87% carbon 11-14% hydrogen, 0.1-3% oxygen, 0.1-1.0% nitrogen and 0.1-8% sulfur by mass with trace elements such as vanadium, nickel, iron, and copper present at the part per million (ppm) level. [6]

Presently, biofuels are only suitable for certain applications or need to be subjected to upgrading processes. Currently, the most suitable use of biofuels is as a replacement to heavy fuel oil industrial boilers [12,13]. Boilers can generally handle a wide variety of fuels, so HTL bio-oil would be suitable if had acceptable emissions, consistent characteristics and made sense economically [5]. The use of bio-oils to replace heavy fuel oils in boilers is already proven, and there is an ASTM burner fuel standard for fast pyrolysis oil (ASTM D 7544). As of 2013, several companies are planning to commercialize bio-oil production for use in boilers [12]. The next steps are to replace light fuel oil for boilers and then gas turbines, diesel engines and transportation fuels. The European Committee of Standardization is currently working to create standards for some of these biofuel applications [5].

Some dissimilarities between bio-oil and petroleum cause bio-oil to still be unsuitable for light-oil boilers, turbines and engines. Most analysis on bio-oil compatibility have been centered around introducing fast-pyrolysis oils into current infrastructure, which are expected to have similar issues as HTL derived bio-oil since they come from similar initial biomass feedstocks. Fast-pyrolysis oils are composed of about 54-58% carbon, 5.7-7.0% hydrogen, 35-40% oxygen and 0-0.2% nitrogen by mass with a negligible sulfur content [5]. The main issue with the fast-pyrolysis bio-oil is its high oxygen content, which is the primary cause of differences in properties from traditional crude oil [5]. These

differences include high water content, a wide range of boiling temperatures, viscosity increase with time, high acidity, higher ignition temperatures and lower heating values [5]. Bio-oil produced from HTL varies in composition depending on the biomass feedstock and process conditions, but like fast-pyrolysis bio-oil, it generally has high oxygen and nitrogen contents compared with crude oil, and is therefore likely to also suffer from the issues listed above [6,15,16].

2.4 Batch Reactor Studies

Hydrothermal liquefaction has been carried out in small batch reactors by several groups. These batch experiments can help characterize the optimal feedstock and process conditions before building a continuous system and/or scaling up. Although several groups have conducted batch experiments with algal biomass, very few HTL experiments have used municipal sludge or biosolids. In batch HTL experiments by Suzuki et al. (1988), digested biosolids, waste activated sludge, raw sludge, and a waste activated-raw mixture were loaded with different levels of sodium carbonate catalyst [1]. The biomass was heated to a maximum temperature of 300°C at an unspecified heating rate and then immediately cooled. The initial sludge type had very little effect on the resulting oil composition. All four sludge types gave values of 69.6-71.4% carbon, 8.8-10.5% hydrogen, 5.6-7.5% nitrogen and 12.4-15.1% oxygen which all resulted in higher heating values of ~34-37 MJ/kg. The raw sludge resulted in the highest yield of 44% with an HHV of 34.5 MJ/kg while the raw and waste activated mix resulted in the best HHV of 36.9 MJ/kg with an average yield of 42%. The digested sludge had the worst yield of 25% with a HHV of 34.2 MJ/kg. The study also concluded that catalyst loading was unnecessary as it had no significant effect on yield or oil properties. [1]

In a batch experiment by Vardon (2011), anaerobically digested biosolids were subjected to a reaction temperature of 300°C for 30 minutes with an unspecified heating rate [2]. The yield was 9.4% with an HHV of 32 MJ/kg [2]. Neither of the previous studies on sludge and biosolids tested the effect that process conditions had on the yield or composition of the oil.

Other batch HTL studies have been conducted with livestock manure. Yin et al. (2010) used cattle manure and tested the effect of reaction temperature, process gas, initial pressure, residence time, and solids percentage on oil yield [17]. Yields were maximized at a reaction temperature of 310°C and with a CO_2 as the process gas. Increasing pressure decreased the oil yield. Residence time at the reaction temperature had no effect on yield from 0 to 15 minutes but greatly reduced yield at longer residence times. A biomass slurry with 20% solids resulted in a 49% oil yield, but slurries with 33% and higher solids percentages had drastically reduced oil yields of <10%. The highest yield across all experiments was 49% at 310°C with CO_2 at atmospheric pressure as the process gas, 15 minutes of residence time and 20% solids. For these conditions, the composition was 73.72% carbon, 8.13% hydrogen, 1.39% nitrogen and 16.76% oxygen to give a HHV of 33.5 MJ/kg. The composition was not tested for other process conditions. [17]

He et al. (2000) conducted experiments with swine manure and varied several parameters including the reaction temperature, residence time and solids percentage [16,18,19]. All experiments used carbon monoxide as the process gas and had a heating rate was 5~10°C /min. The optimal temperatures were between 285°C and 350°C, and oil was not consistently yielded at 275°C [18]. Residence times were varied from 5 to 120 minutes and showed different trends in oil yield depending on the reaction temperature [18]. Tests at 285°C showed increasing yield with increasing residence time, while tests at 295°C and 305°C did not show a consistent trend but always had between 60% and 80%

oil yield [18]. The compositions were only found for three of the tests. At 305°C, 120 minute residence time and 20% solids, the oil had highest HHV of 38.5 MJ/kg and a composition of 77.9% carbon, 9.4% hydrogen, 4.6% nitrogen and 7.0% oxygen [16].

Algae feedstock has been the most thoroughly studied biomass type for HTL conversion. Although it is not compositionally as similar to municipal biosolids as livestock manure, some trends may carry over. Yu et al. (2011) showed that changing the pressure had no effect on the bio-oil yield [20]. Several studies have demonstrated that oil yield is highly dependent on temperature and independent of residence time with optimal temperatures of 300-350°C and tested residence times varying from 1-120 minutes [10,15,20].

Experiments by Faeth et al. (2013) indicated that very high heating rates (~200°C/min) and low residence times (1-5 min) produced high bio-oil yields [15]. A batch reactor containing the algae strain *Nannochloropsis* was heated in a sand bath that was set between 300 and 600°C in order to control the heating rate. The reactor was held in the sand bath for either 1, 3 or 5 minutes and then immediately quenched. The highest yield of 66% was achieved when the biomass was heated at 600°C for 1 minute and only reached a temperature of approximately 300°C before being quenched. For this test, the elemental composition was 70.58% carbon, 9.00% hydrogen, 6.92% nitrogen, 0.74% sulfur and 12.75% oxygen with a HHV of 34.51 MJ/kg. Exact trends in the yield and HHV were difficult to track in this experiment because the max reactor temperature was different for every test and often exceeded 374°C, at which point water was no longer subcritical, and HTL could no longer occur.

Based on literature for livestock manure and algae, it was determined that the optimal reaction temperature for municipal solids was 310-335°C. The optimal residence time and solids loading were not clearly defined as conflicting trends were observed in

different papers and at different temperatures. The heating rate had barely been explored for algae and never been considered for municipal sludge or biosolids.

2.5 CONTINUOUS HTL REACTORS

Continuous HTL systems have been built and tested by the government, by research institutions and private companies over the last several decades. These systems vary substantially because each converts a different type of biomass and serves a different purpose. The first continuous systems in the 1970s converted woody biomass as a large scale demonstration, but more recently, continuous systems have been built for research purposes, mostly to convert algae.

The first continuous system was a demonstration scale plant in Albany, OR which was scaled up from laboratory testing at the Pittsburgh Energy Research Center (PERC) and the Lawrence Berkeley National Laboratory (LBNL) in order to collect data necessary for industrial scaling and construction of HTL. The first system processed 7 to 10 wt% wood in oil-based slurry with sodium carbonate catalyst through an electrically heated reactor with mixing blades and a separate vessel introducing reducing gases. The stirred reactor often plugged and was redesigned. The stirred tank was replaced with high pressure tubing that ran through a furnace and an upflow tubular reactor that held the slurry at temperature and pressure for an extended period. This design is shown in the Figure 2.1. Both systems utilized a low pressure and then a high pressure pump in series. The plant successfully demonstrated the HTL process by producing 35 barrels of oil at about 70 pounds of wood per hour. With the HTL process proven and the demand for oil dropping, the project concluded in 1981. [9]

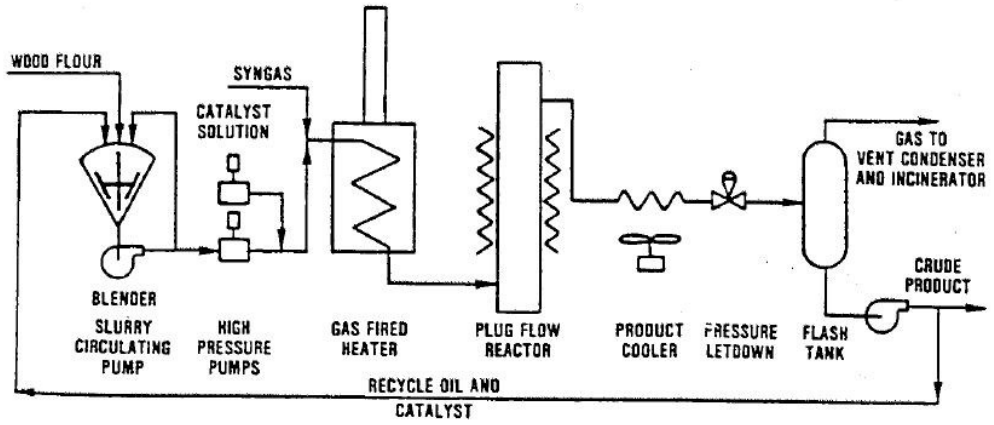

Figure 2.1: Schematic for Albany test facility.

LBNL continued HTL work with a laboratory-scale system with the main focus of determining the effect of using an aqueous slurry versus and oil-based slurry. LBNL developed a continuous bench-scale continuous system that utilized a high pressure pump (Monyo), and a 1 L stirred autoclave reactor. The system operated at 350°C with a 10-30 minute residence time. The project was discontinued in 1983. [9]

In the 1980s, a continuous system was built at the University of Arizona system for the purpose of pumping slurries with high solids percentages (up to 60 wt%) by using an extruder. The extruder was a helical screw rotating around a cylinder to move viscous fluids through a channel. Slurries were fed to the extruder using a cram-feeder, heated and pressurized to 150-200 °C and 33MPa (4800psi) in the extruder, and then pumped through an externally heated vertical reactor at 200atm and 310-350 °C for 35-50 minutes. The system converted up to 20 kg/hr of 45-60 wt% slurry. The program ended in 1988 [9].

In the 1980s the EPA Water Engineering Research Laboratory conducted an HTL project with sludge as the biomass feedstock and branded it as a sludge-to-oil reactor system (STORS). The STORS continuous system used a 15cm O.D., vertical stirred tube with sludge entering via an injection pump. The unit was heated with a 21.4kW ceramic

heater. The system could process up to 20% solids and 30 L/hr of slurry. A set point temperature of 300 ℃ and residence time of 1.5 hours was used. [21]

HTL research was dormant for most of the 1990s and 2000s, and it wasn't until 2013 that continuous systems were built at a laboratory scale by Jazrawi et al. (2013) at the University of Sydney and Elliot et al. (2013) at the Pacific Northwest National Laboratory (PNNL) [10,11]. The system by Jazrawi et al. was a microalgae HTL system consisting of two pumps, coil in shell heat exchangers for preheating, a tubular coiled reactor submerged in a fluidized sand bath for primary heating and the same heat exchangers for cooling. The diagram is shown in Figure 2.2. The first pump (type Range MD; Seepex, Germany) pump provided the necessary suction of 2-6 bar, and the second pump (model Ariete NS3006P; GEA Niro Soavi, United Kingdom) operated up to 600 bar with flow rates of 15-90 L/h and could handle high viscosity fluids. The primary heating reactor consisted of four 316 stainless steel tubing sections, each 16 m in length, with a 9.5 mm OD, 1.65 mm wall thickness and 2 L total reaction volume. The coils were submerged in the sand bath, which was heated by four 6 kW electric heating elements. The system operated successfully for several testing runs, however, it could not process any slurry with greater than 10wt% algae because the control valve orifice became blocked. The reactor tubing itself was never blocked. At lower temperatures there were significant pressure fluctuations due to blockage of the control valves. At higher temperatures, more of the algae were converted into smaller particle size product, limiting blockage and pressure fluctuations. [10]

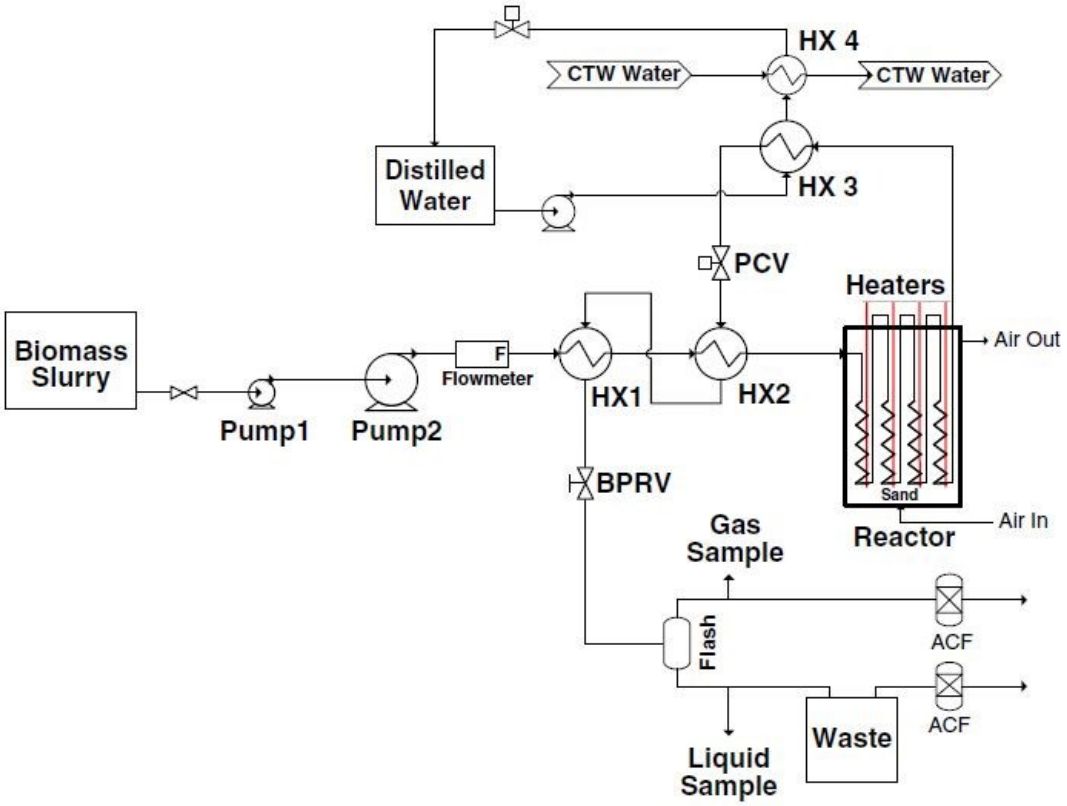

Figure 2.2: Schematic for continuous system by Jazwari et al. (2013).

The continuous system at PNNL was modified from a continuous catalytic hydrothermal gasification system. It used a high pressure pump feeding system, a 1 L stirred tank reactor, a 1 L tubular reactor, a solid separator, two collection vessels and continuous venting. A diagram of the system is shown in Figure 2.3. For two of the four tests, a shell and tube heat exchanger was also added to preheat the slurry to 133 °C and a spacer was added to reduce the volume of the reactor to 400mL. The design was based on a feed rate of 1.5 L/h of slurry and a typical continuous test period of 6-10 hours. The pumps were dual syringe pumps (model 500D; Teledyne ISCO, Lincoln, NE) that alternated pumping to provide continuous flow. The reactor vessel (Inconel) equipped with internal stirring propellers and functioned as a back-mixed reactor. Additional residence

time was provided with a plug flow reactor. After the plug flow reactor, a combination settler filtered solids out to the bottom of the vessel where they could be removed. Products could then be directed to one of two collection vessels as the inactive vessel was emptied. Gas byproduct was continuously vented. [11]

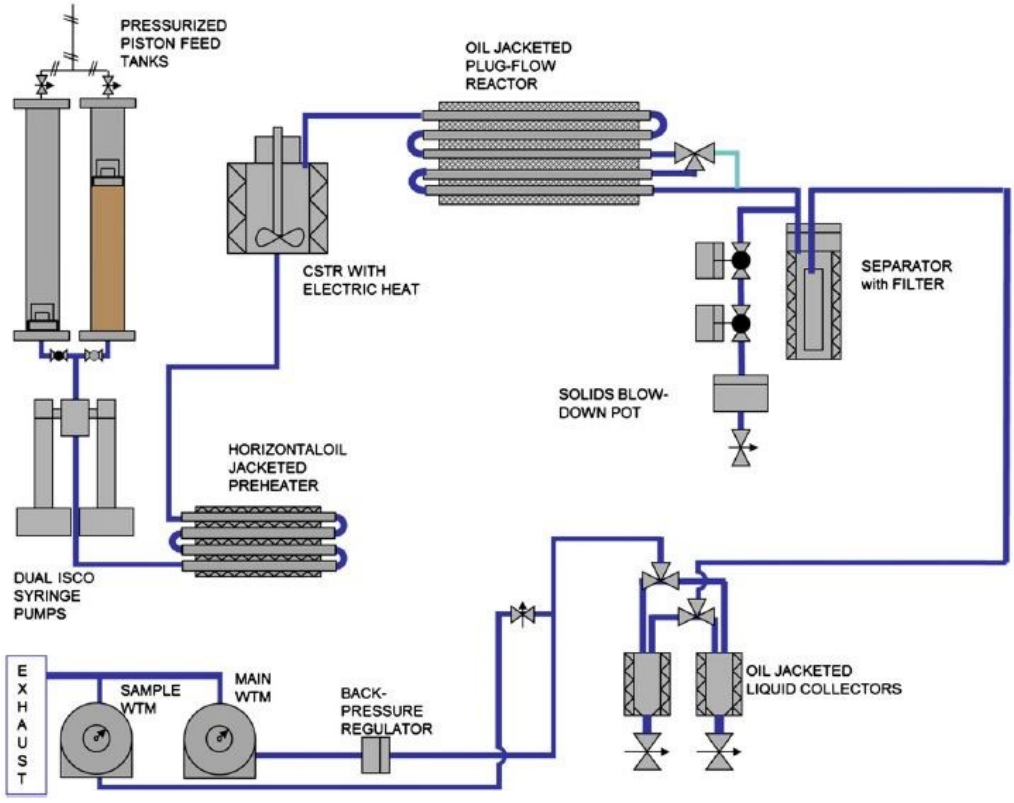

Figure 2.3: Schematic of continuous system by Elliot et al. (2013).

In addition to the work published by Elliot et al. and Jazwari et al., a few companies may have recently developed continuous or semi-continuous HTL systems; however, their work is mostly proprietary. Algenol, Muradel and Sapphire Energy have developed demonstration scale systems although the details are generally unknown.

Chapter 3: Effects of Heating Rate, Residence Time, Feedstock Solids Concentration and Feedstock Type on Conversion Yield and Higher Heating Value of Bio-Oil

3.1 Introduction

This chapter presents an experimental study to assess the effects of residence time (RT), heating rate (HR), feedstock solids percentage (SP) and feedstock type on the oil yield and composition during the conversion of municipal sludge and biosolids into bio-oil using batch HTL reactors. To the best of our knowledge, this is the first study to explore the effects of residence time, heating rate or solids percentage for the HTL of sludge or biosolids.

3.2 Materials and Methods

3.2.1 Feedstock

Sludge and biosolids samples were obtained from the Hornsby Bend Biosolids Management Plant in Austin, TX. The Hornsby Bend Plant influent is a mixture of sludge outputs from two wastewater treatment plants. The sludge mixture is dewatered with the aid of Zetag 8819, a cationic emulsion polymer, and then sent to anaerobic digesters. After digestion, more Zetag 8819 is added, and the feedstock is further dewatered into a thick cake that can be used as a component in compost or as a fertilizer. The samples for this study were taken just before anaerobic digestion (hereafter called pre-digestate), just after anaerobic digestion (hereafter called post-digestate), and after the final dewatering stage (hereafter called dewatered).

Table 3.1 shows the properties of the samples used in the experiments. Separate studies were carried out at different times of the year and with different samples from Hornsby Bend. Because of temporal changes in the incoming sludge, samples taken from the same location had different properties for each study. A number in parentheses is used

to name and keep track of each feedstock. The addition of polymer and the slight difference in sampling location did not cause dewatered (2) to be compositionally different from post-digestate (2), and so from this point on, the dewatered biosolids are considered to be a part of the post-digestate category. The moisture content and the organic content of each sample were measured by finding the mass lost when baking the samples in a muffle furnace at 80°C to remove moisture and at 540°C to remove organics. Samples were sent to Atlantic Microlabs (Norcross, GA) for analysis after drying at 80°C to determine the composition. All samples were stored at 4°C for a maximum of 5 days before testing in order to prevent biological changes, including further degradation by the microorganisms used for anaerobic digestion.

Feedstock Type	Solids [wt%]	Organics in Solids Portion [wt%]	C [wt%]	H [wt%]	N [wt%]	S [wt%]	O [wt%]
Pre-digestate (1)	6.3	84.3	42.6	6.3	5.4	0.8	44.9
Pre-digestate (2)	6.3	75.9	40.2	5.9	5.2	1.0	47.8
Post-digestate (1)	3.2	68.4	33.1	4.7	4.6	1.9	55.7
Post-digestate (2)	4.7	60.2	31.0	4.2	3.9	1.4	59.4
Dewatered (2)	18.2	58.5	31.3	4.2	3.9	1.5	59.0

Table 3.1: Feedstock properties.

3.2.2 The Batch Reactor

The batch reactor, pictured in Figure 3.1, was constructed from a ¾" union (SS-1210-6; Swagelok, Austin, TX), ¾" plug (SS-1210-P; Swagelok) and bored through reducer, ¾" to ¼" tube (SS-400-R-12BT; Swagelok). A type K thermocouple (101-K-U-C-2-C; Ultra Electronics, Austin, TX) was swaged into the reducer to measure temperature during testing. The working volume of the reactor was 8.5mL. For all tests, the reactor was loaded with 3.50±0.08 grams of slurry.

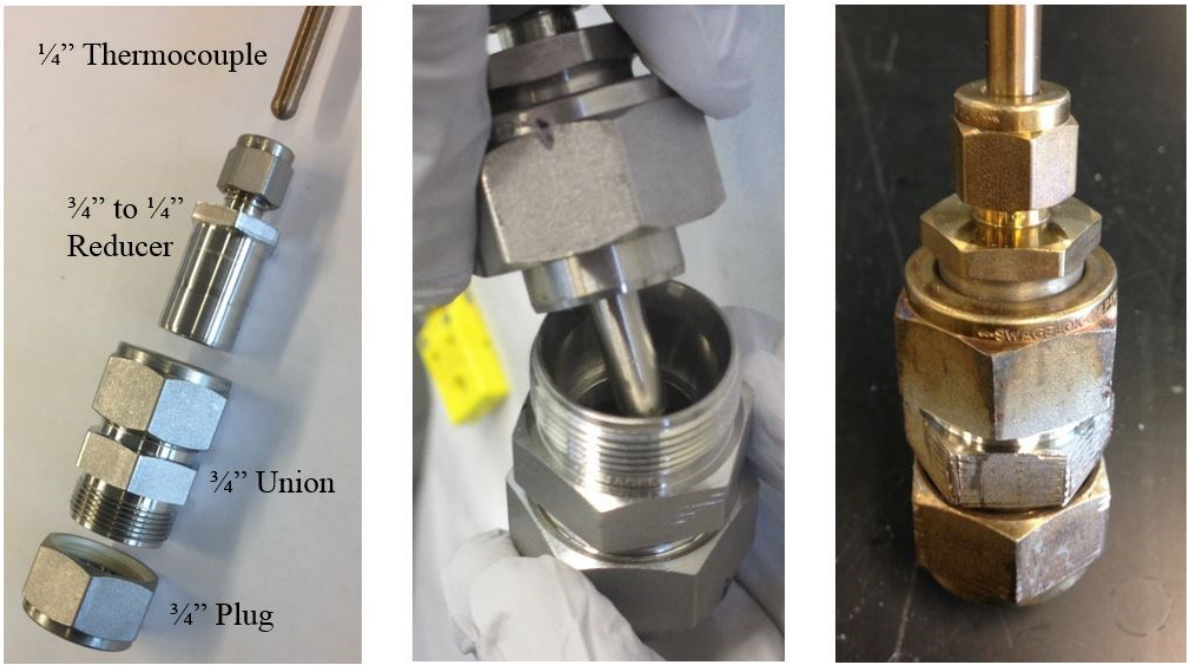

Figure 3.1: The batch reactor. (left) The disassembled reactor, (middle) the assembled reactor before closing, (right) and the assembled and closed reactor prepared for heating.

A preheated fluidized sand bath (Model SBS-4; Techne Calibration, Burlington, NJ) was used to rapidly heat the reactor to its specified reaction temperature of 325°C. The sand bath was set to a specified temperature between 400-600°C, which determined the reactor's heating rate. Once the slurry reached its reaction temperature, the reactor was moved to a furnace (Model 180; Hardin Industrial Tools, Goleta, CA) that held the reactor at its reaction temperature of 325°C for the remainder of the specified residence time. Finally, the reactor was cooled to the ambient temperature by quenching in a 5 gallon water bath at 23°C.

3.2.3 Recovery and Analysis of Products

The products of the reaction were recovered from the reactor by rinsing with 10mL of dichloromethane (DCM). The resulting mixture was filtered with a 2.0µm pore diameter

syringe filter unit (SLAP02550; EMD Millipore, Billerica, MA) to separate the solids. After the solids were removed, the aqueous phase and organic phase spontaneously separated and were then pipetted into separate containers. The organic phase was left at atmospheric conditions until its mass was stabilized over several hours, which indicated that the DCM had fully evaporated. The remaining material was considered to be the bio-oil. The oil yields in this paper correspond to the mass of recovered oil divided by the mass of the dried, ash-free biosolids.

An ultimate analysis was performed on each feedstock and bio-oil by Atlantic Microlabs for carbon, hydrogen, nitrogen and sulfur. The oxygen was calculated by difference. The higher heating values (HHV) for each bio-oil sample were then calculated with the Dulong formula using the weight percentages of each element [22]:

$$0.338C + 1.428(H - O/8) + 0.095S = HHV\ (MJ/kg)$$

The uncertainties in the yield and composition were both dominated by the precision uncertainty. The error reported by Atlantic Microlabs was ±0.3%, and bias error due to oil being lost as a result residue left in the reactor, material transfer or filtering was ~0.1%. These errors were both an order of magnitude lower than precision errors and were thus disregarded. The precision error was calculated by multiplying the standard deviation by the student t-parameter for a 95% confidence interval and dividing by the square root of the number of samples.

3.2.4 Design of Experiments

The goals for the study were to assess how heating rate, residence time, solids concentration and biomass type affected the oil yield and composition. The parameters were to be tested as follows:

1. Test three different residence times with consistent reaction temperature and heating rate
2. Test the effect of heating rate by using three different sand bath temperatures with consistent reaction temperature and residence time
3. Test three different solids percentages at identical process conditions
4. Test two different biomass types at the same solids percentage and process conditions.

The residence time was considered to be the time that the biomass spent above 200°C, which is approximately where hydrothermal liquefaction reactions begin to take place [3]. Each experiment was completed at least in duplicate.

Heating Bath Temp (°C)	Residence Time (min) 4	10	25	Solids Percentage
600	X			6.2%
450	X	X	X	
350	X			
600				4.1%
450	X			
350				
600				1.1%
450	X			
350				

Heating Bath Temp (°C)	Residence Time (min) 4	8	12	Solids Percentage
600	X			3.4%
450	X	X	X	
350	X			
600				6.2%
450	X			
350				
600				10.8%
450	X			
350				

Table 3.2: (left) DOE for pre-digestate (1), and (right) DOE for post-digestate (1). X's indicate the experiments that were performed.

Table 3.2 shows a design of experiments (DOE) for the pre-digestate (1) and post-digestate (1) testing. The pre-digestate (2), post-digestate (2) were only tested at 6.2%

solids and 4 minutes residence time at two different heating rates. A test with the dewatered (2) was conducted and considered in the results as the post-digestate (2) with a high solids percentage.

3.3 Results and Discussion

3.3.1 Effect of Separation Methods on the Reliability of Results

The largest issue throughout the batch experiments was separating the oil from the aqueous and solids phases. Previous literature offered several different methods of phase separation, some of which produced more consistent and reliable results than others.

The first method we tried had been developed by Valdez et al. (2012) and also used by Faeth et al.(2013) [15,23]. After HTL, the reactor contents were poured into a glass conical tube and the inside of the reactor was rinsed with dichloromethane, which was also added to the same tube. The oil phase was dissolved in the DCM. The tube was centrifuged to induce phase separation with DCM below the aqueous phase. Solids resided below the DCM and also at the interface of the DCM and aqueous phases. The DCM phase was transferred to a separate vial using a glass pipet and the oil was the leftover material after the DCM evaporated. The main issue encountered with this method was that it was difficult to consistently pipette the full amount of dichloromethane without mistakenly obtaining solids. When the pipet tip contacted the layer of solids at the interface, solids would often spray into the DCM phase and mistakenly be obtained for the final oil sample. Also, the last bit of DCM was difficult to pipet as it resided between the two solids layers. As a result, samples obtained in this method did not show consistent oil yields for the same testing conditions.

An alternative method used by Suzuki et al. (1988) and Barreiro et al. (2013) was to remove solids by filtration [1,24]. Suzuki et al. used 5 μm filter paper (5C; Toyo Roshi

Co., Japan) while Barreiro et al. used 1 μm pore size glass microfiber filter (GF/B; Whatman PLC, Little Chalfont, UK). Both used DCM to rinse the products from their reactors, but Barreiro et al. filtered all reactor products together while Suzuki et al. separated the aqueous phase out before using filter paper. Initially, we set up a vacuum filter with a fritted glass funnel and 5 μm polypropylene filter paper (3609L Midwest Filtration, West Chester Township, OH). When the DCM and aqueous phases where filtered together, a small amount of solids was still present, however, the two liquid phases spontaneously separated. The remaining solid particles existed at the liquid interface or floated in the DCM phase. When the DCM was pipetted and filtered again, some solid particles were still visible. Different vacuum strengths were tested, but a small amount of solids were always visible after filtering. The 5μm paper was deemed to have too large of a pore size, and so a 2μm glass fiber syringe filter (SLAP02550; EMD Millipore) was used next. The 2μm filter was capable of filtering out all solids. In tests with high quantities of solids, it was necessary to push the mixture through with a larger force that allowed some solids through on the first pass. After a second filtration, all solids were removed. For consistency, all samples were filtered twice. The filtered mixture spontaneously separated and the DCM was pipetted into a separate container. After the DCM evaporated, the oil remained. This final method yielded consistent results.

Because only the first two method yielded inconsistent results, experiments conducted using these methods were deemed unreliable for determining conversion yields. However, the composition data was not affected by these inconsistencies and were still valid. Thus, in the results presented below, yield data is only reported for the pre-digestate (1) and HHV is reported for all biosolids types.

3.3.2 Effect of Residence Time

The residence time was varied between 4 and 25 minutes at a constant reaction temperature of 325ºC and heating rate of 270ºC/min with 6.2% solids in the feedstock. Figure 3.2 shows representative temperature profiles for residence times of 4, 10 and 25 minutes. The residence time was defined as the time above 200ºC, which is approximately where HTL reactions begin [3].

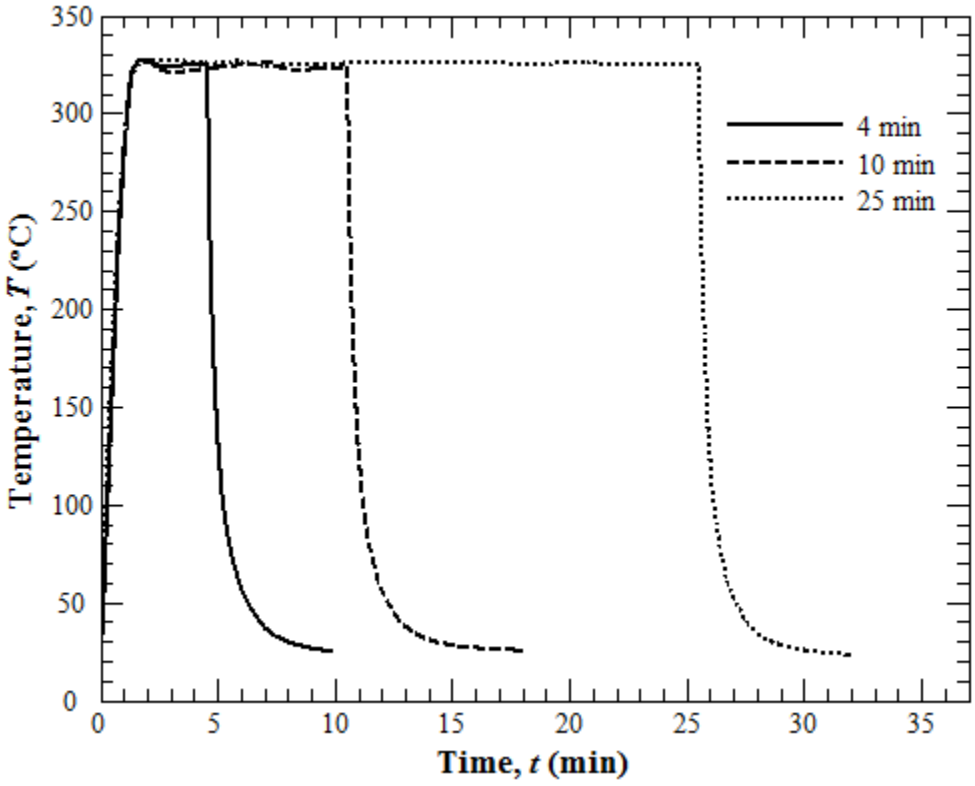

Figure 3.2: Characteristic temperature profiles for residence times of 4, 10 and 25 minutes at a constant reaction temperature of 325ºC and heating rate of 270ºC/min with 6.2% solids in the feedstock.

Figure 3.3 shows that HHV was unaffected by changes in residence time. All but one data point showed HHV uncertainties of less than 1 MJ/kg; however, a single data point had an inflated uncertainty of 4.62 MJ/kg. For this data point, only two identical tests

were valid because the third test used the incorrect initial mass, so the data was discarded. The test was not re-run because the biosolids may have changed significantly in the several days between the test and the recognition of the error. There is a clear discrepancy in the bio-oil HHV based on the feestock type. This issue is described in detail in Section 3.4.4.

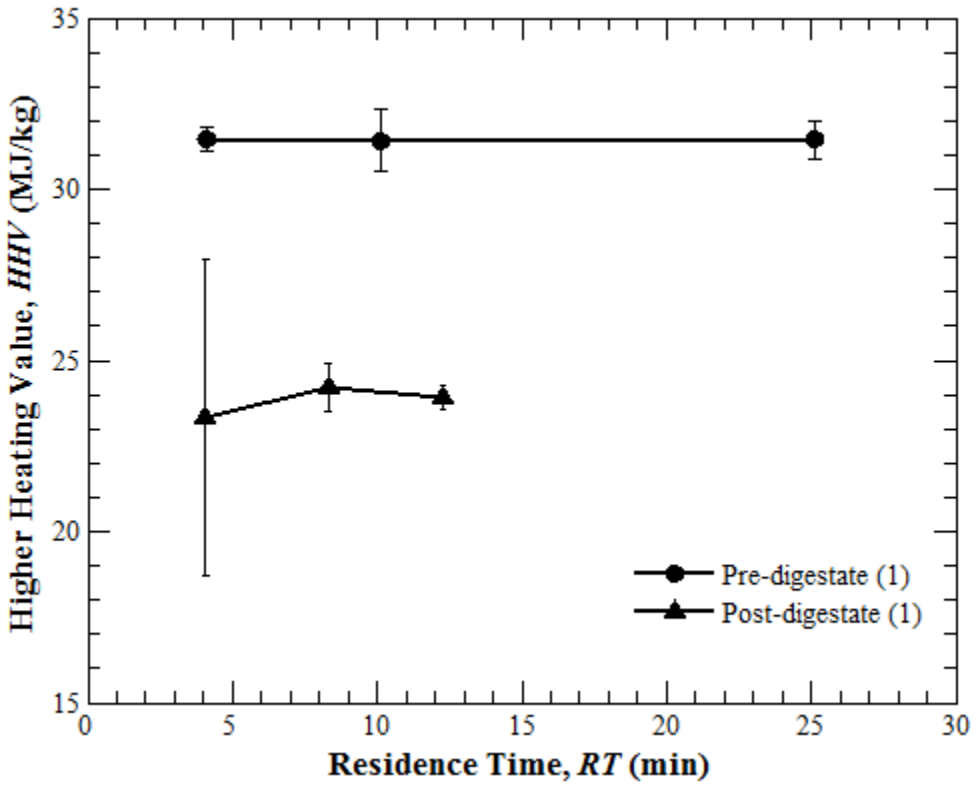

Figure 3.3: Effect of residence time on HHV at a constant reaction temperature of 325ºC and HR=270ºC/min and 6.2% solids.

Figure 3.4 shows that bio-oil yield was unaffected by residence time. No post-digestate yields were found due to the filtering issues described in Section 2.3.1. The literature reports that at insufficient residence time HTL reactions will be incomplete, and at excessive residence times the bio-oil products will be overoxidized and form char [17,18,25]. It can be hypothesized that the pre-digestate sludge in this experiment was

completely converted at 4 minutes and still did not overoxidate up to 25 minutes. This lack of degradation is interesting as compared with Yin et al. (2010), who reported a sharp decline in yield between 15 and 20 minutes (with residence time considered to be the time at the reaction temperature) when processing cattle manure at 315ºC. The bio-oil created by the Hornsby Bend sludge seems to be more stable than Yin's cattle manure because it was exposed to harsher process conditions and still did not overoxidate. Oxidation generally occurs when fatty acids are exposed to oxygen, especially at higher temperatures [26]. This may indicate that the sludge-derived bio-oil has lower fatty acid content and therefore a higher oxidative stability. While the lack of fatty acids may cause increased stability, it also may help explain why Yin et al.'s bio-oil had a higher HHV of 35.52 MJ/kg (on average) than the 31.4 MJ/kg average for pre-digestate (1) found in this study. A forage analysis of the initial feedstocks and a gas chromatography-mass spectroscopy (GC-MS) analysis of the bio-oil may verify these hypotheses and also help determine how the feedstock and residence time relate to oil stability and yield.

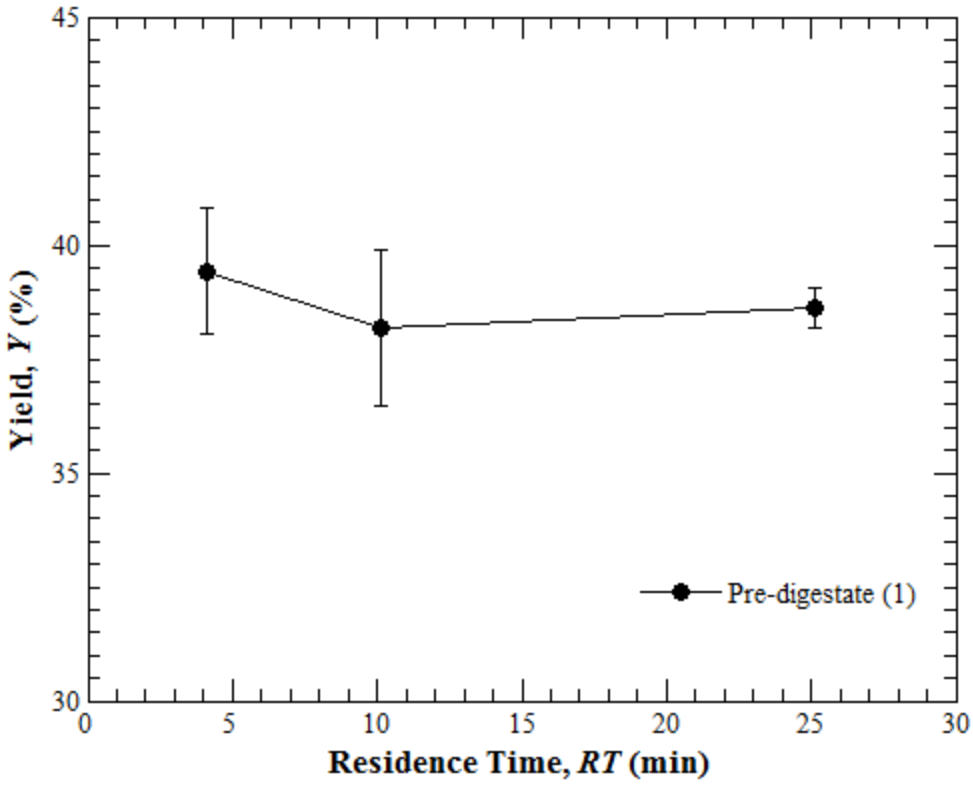

Figure 3.4: Effect of residence time on conversion yield at a constant reaction temperature of 325ºC and HR= 270ºC/min and 6.2% solids.

3.3.3 Effect of Heating Rate

The heating rate was varied from 130ºC/min to 508ºC/min with a constant reaction temperature of 325 ºC and residence time of 4 minutes with 6.2% solids in the feedstock. Figure 3.5 shows characteristic temperature profiles for these experiments at heating rates of 130ºC/min, 270ºC/min and 380ºC/min. This figure shows that the temperature profiles are not linear, and so the heating rates are not constant values. So that comparing heating rates could be done easily, a representative value was taken as the average heating rate between 100°C and 250°C, where the profile is most approximately linear.

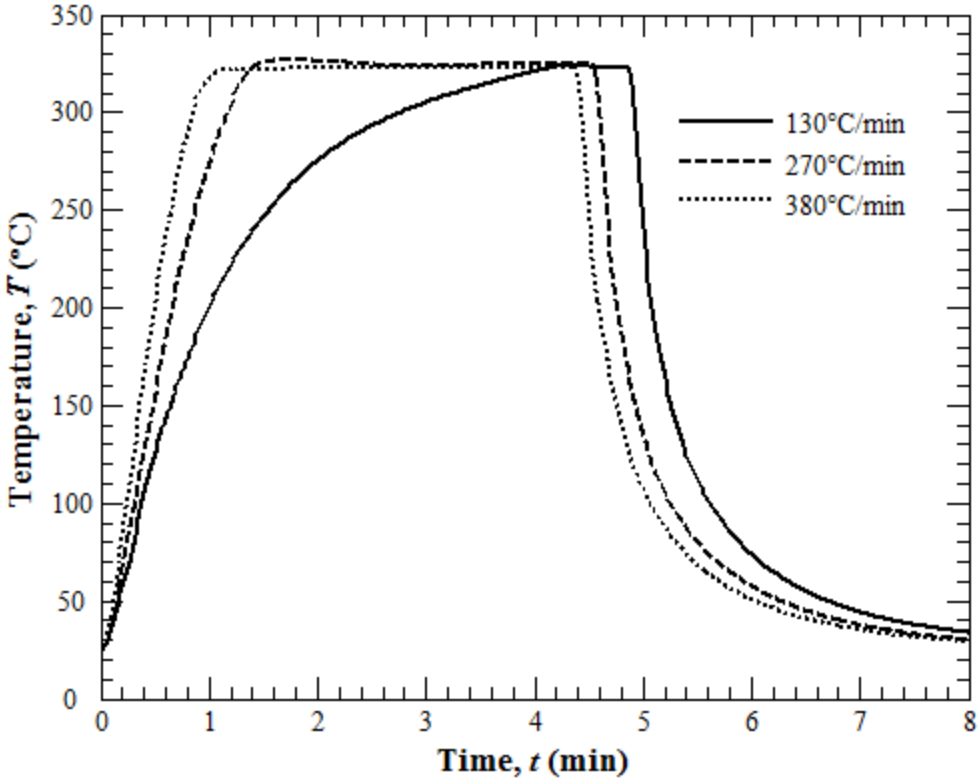

Figure 3.5: Characteristic temperature profiles for heating rates of 130ºC/min, 270ºC/min and 380ºC/min at a constant reaction temperature of 325ºC and RT=4 min with 6.2% solids.

Figure 3.6 shows the effect of heating rate on the HHV. Regardless of biosolids type, the HHV did not show any statistically significant variation at different heating rates. This indicates that approximately the same reaction pathway occurs and the same types of bio-oil compounds are created regardless of the heating rate.

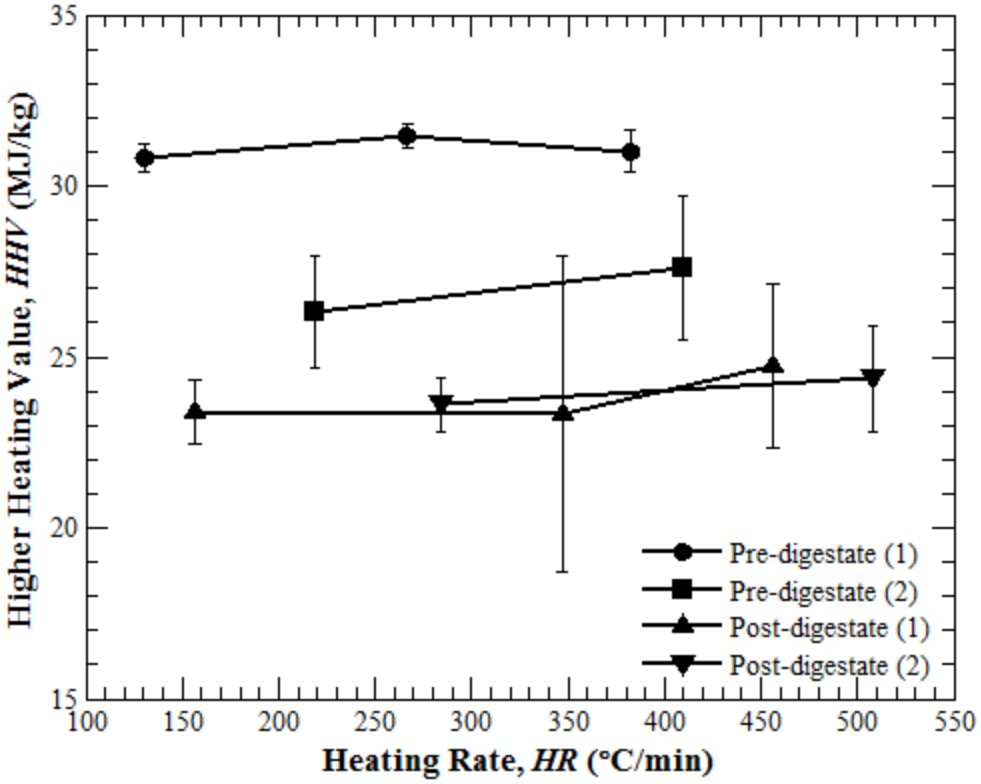

Figure 3.6: Effect of heating rate on HHV at a constant reaction temperature of 325ºC and RT= 4 min with 6.2% solids.

Figure 3.7 shows how bio-oil yield is related to heating rates. The oil yield peaks at the midrange heating rate of 270°C/min. This trend in does not match the trends reported by Faeth et al. (2013) that showed greatly increased oil yield as heating rate was increased from 70ºC/min to its maximum value of 300ºC/min for algal HTL [15]. Faeth et al. attributed the observed trends to either the lysing of algal cells or more optimal reaction kinetics at higher heating rates [15]. Although this study cannot provide any insight concerning algal cell lysing, the compositional differences of algal biomass and sludge could explain the differences in the trends observed. First, *Nannochloropsis*, the strain of algae used by Feath et al., is primarily composed of proteins (~50%) and lipids (~30%),

whereas sludge and biosolids are less consistent in composition, but generally composed of high amounts of cellulose and hemicellulose (~25-60%) [1,2,27]. The simplified hydrothermal liquefaction reactions are hydrolysis/depolymerization of the biomass, decomposition of the biomass monomers and reformation of the decomposed fragments [28]. Protein is linked by strong peptide bonds, so it does not depolymerize nearly as easily cellulose and hemicellulose at temperatures below ~250°C [29]. As temperatures reach ~290°C and above, the amino acids released during protein polymerization are quickly degraded. At 290°C, the peak amino acid yield occurs at about ~2 minutes before rapid degradation takes place [29]. For the purposes of HTL, these degradation reactions are not necessarily optimal as evidenced by higher yields being reported for reaction temperatures of 300°C-350°C for algal HTL [10,15,20]. The high yields obtained by Faeth et al. at high heating rates may be explained by the fact that unwanted amino acid degradation normally occurs during slow HTL, but a more optimal amino acid release and degradation occurs during fast HTL.

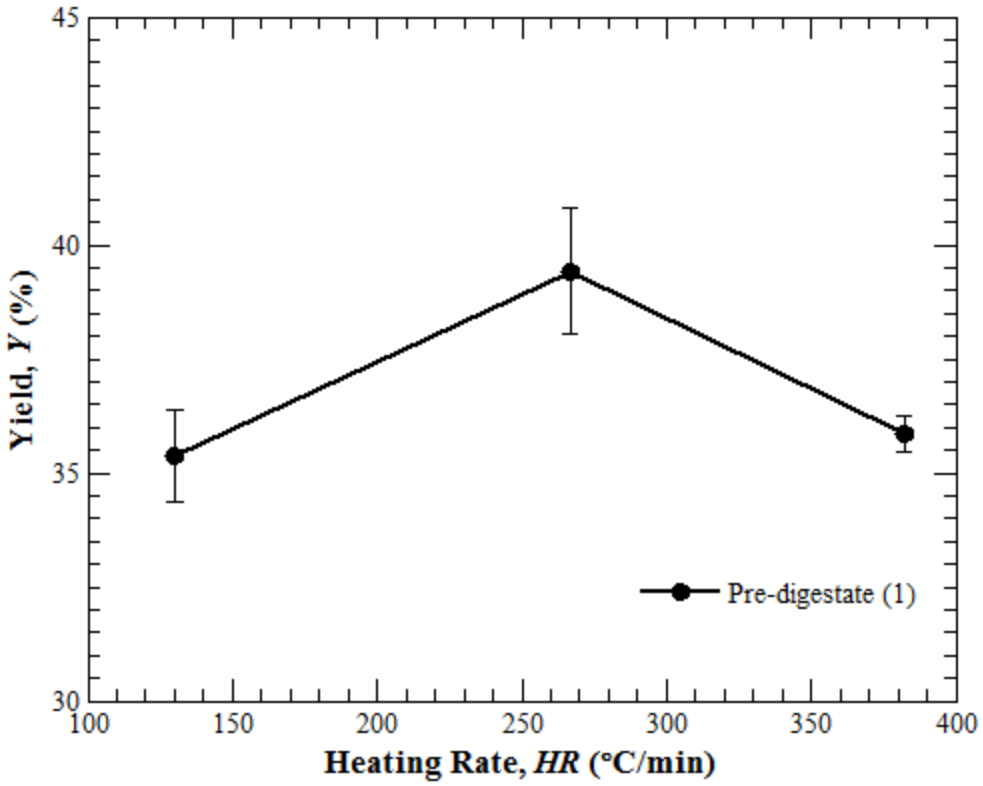

Figure 3.7: Effect of heating rate on conversion yield at a constant reaction temperature of 325ºC and RT=4 min with 6.2% solids.

On the other hand, previous studies show that hemicellulose and cellulose are hydrolyzed into glucose more easily than protein is depolymerized. Hemicellose is easily hydrolyzed at temperatures of about 180°C, and cellulose is fully hydrolyzed in 2 minutes at 280°C [29,30]. At higher temperatures (>320°C), the cellulose hydrolysis rate is higher than the glucose decomposition rate. Because both the hydrolysis and decomposition reactions can occur at a wider range of temperatures, sludge containing high levels of cellulose and hemicelolose may be less influenced than algae by changes in heating rate. These complex reaction kinetics may have influenced the small peak in sludge to bio-oil conversion yield at the midrange heating rate of 270°C/min. In order to further investigate

the why the trends by Faeth et al. differ from these so drastically, it may be useful conduct a forage analysis on several types of biomass feedstocks and process them at the same set of heating rates. Then, the organic matter content of the feedstock and the heating rate could be independently controlled and compared.

3.3.4 Effect of Solids Content

The solids concentration in the initial feedstock was varied and process conditions were held constant with a reaction time of 325°C, and heating rate of about 270°C/min and a residence time of about 4 minutes. Figure 3.8 shows the characteristic heating curve.

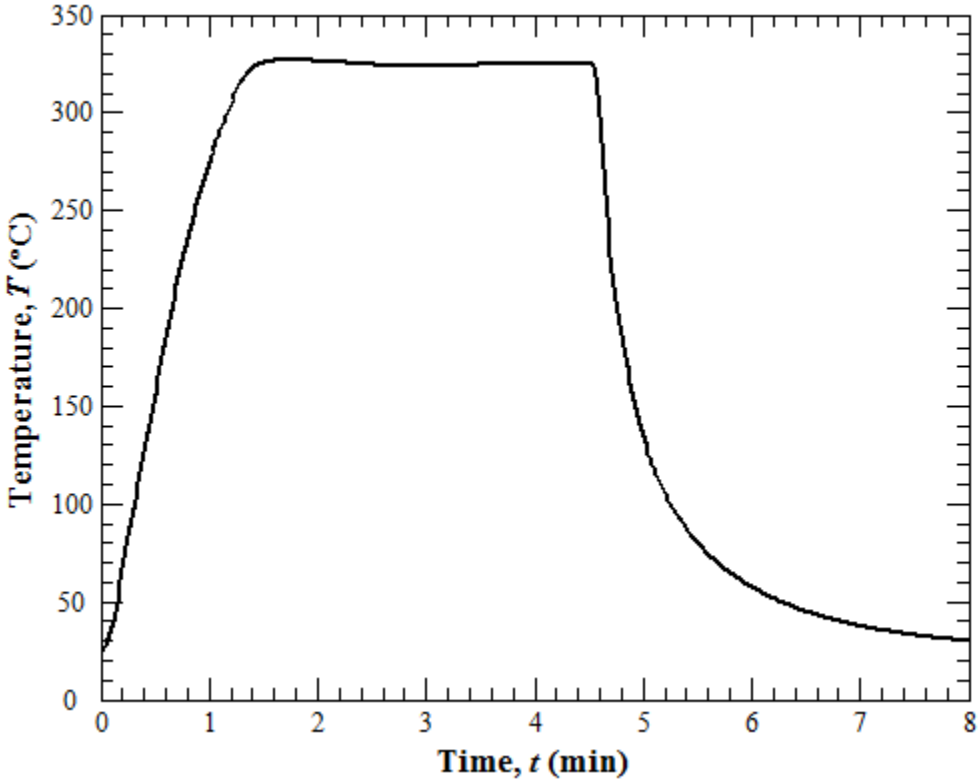

Figure 3.8: Characteristic temperature profiles at a reaction temperature of 325ºC, heating rate of 270 ºC/min and RT=4 min with 6.2% solids.

Figure 3.9 shows the effect that solids content had on the HHV. Clearly, higher a higher solids percentage in the feedstock resulted in a higher HHV in the bio-oil. This trend may be related to the final step of HTL where decomposed organic fragments reform into bio-oil. When the solids content is low and these broken down molecules are surrounded by water, it may be more difficult to for them to bond with other molecules to create long-chain, high-energy hydrocarbons.

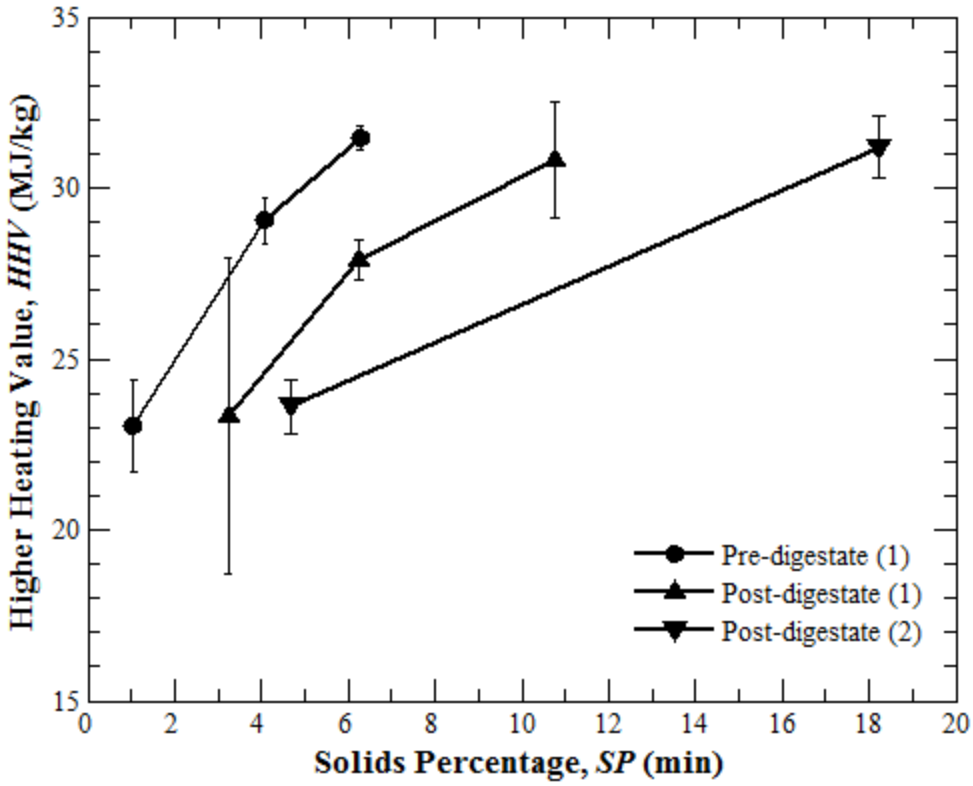

Figure 3.9: Effect of solids concentration on HHV. The process conditions for pre-digestate (1) were 325°C, RT=4 min and HR=270°C/min. Conditions for post-digestate (1) were 325°C, RT=4min and HR=320°C/min. Conditions for post-digestate (2) were 325°C, RT=4.5 m and HR=350°C/min.

Figure 3.10 shows the how the solids content effects the bio-oil yield. The oil yield is reaches a maximum of 83.5% with a 1% solids concentration. At 4% and 6.2% solids

concentration, the yield drops to 39%. The increase in yield at low solids percentages may be a result of more favorable depolymerization reactions, which are caused by the presence of water [28]. So, while more water results in more organic matter being depolymerized and decomposed, it simultaneously inhibits the ability of the broken-down organic molecules to reform into long-chain hydrocarbons. The result is high yields and low HHVs at low solid concentrations.

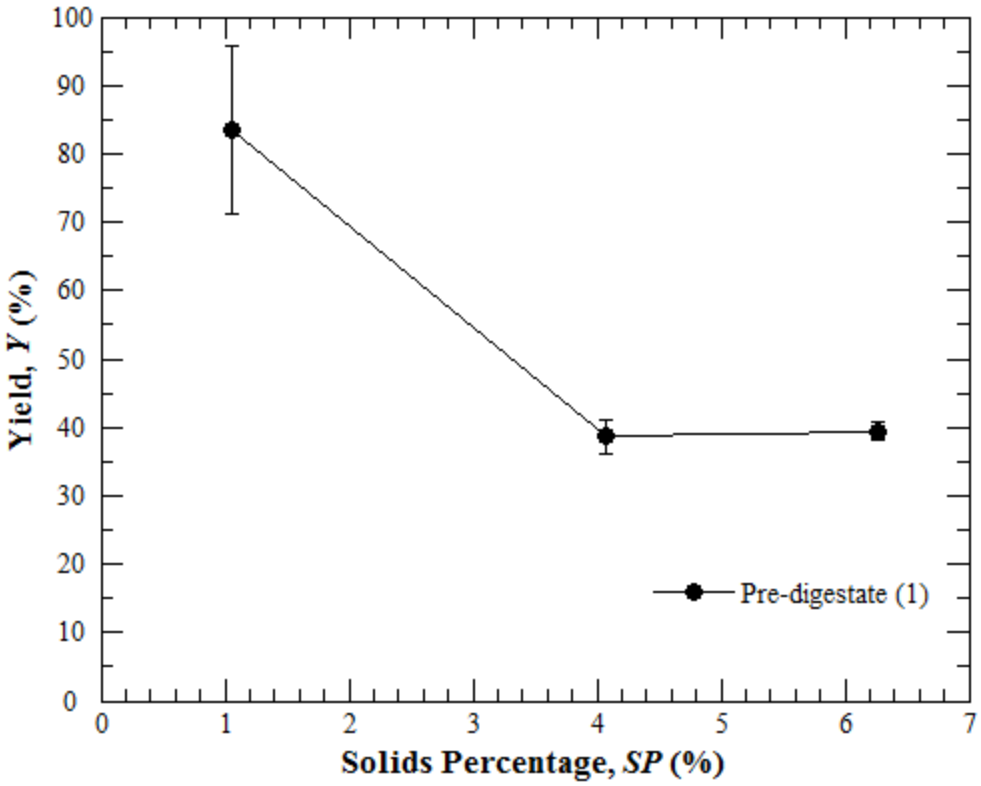

Figure 3.10: Effect of solids concentration on conversion yield. Conditions were 325°C, RT=4 min and HR=270°C/min.

Previous studies on the effect of solids concentration with livestock manure used higher solids concentrations than in this thesis. He et al. (2000) showed that bio-oil yield gradually increased as solids concentration went from 10% to 25% for swine manure [19].

Yin et al. (2010) showed a sharp decrease in yield between 20% and 33% solids and then a constant yield from 33% to 67% solids [17]. The decrease in yield observed by Yin et al. may be attributed to lack of water for depolymerization reactions. The results by He et al., however, do not agree with the trend observed in this thesis and by Yin at et al. A single study that encompasses a wide range of solids percentages (from 1% to greater than 33%) may better explain these reaction kinetics involving water and solids interactions.

3.3.5 Effect of Feedstock Composition

As noted in previous sections, Figures 3.3, 3.6 and 3.9 show that the feedstock type caused a clear difference in the bio-oil HHV. In each of these figures, the lower HHVs corresponded to a higher heteroatom and lower organic percentage in the initial feedstock. In order to further explore this effect, a pre-digestate and post-digestate sample each with 6.2% solids were processed at a reaction temperature of 325°C, a heating rate of 270°C/min and a residence time of 4 minutes. The characteristic temperature profile is the same as shown in Figure 3.8. The initial HHV of the pre-digestate was 15.50 MJ/kg and HTL upgraded it to 31.02 MJ/kg. The post-digestate initially had an HHV of 8.12 MJ/kg and was upgraded to 27.90 MJ/kg. The composition of the resulting bio-oils are shown in Table 3.3.

	HHV [MJ/kg]	**C [wt%]**	**H [wt%]**	**N [wt%]**	**S [wt%]**	**O [wt%]**
Pre-digestate (1) Oil	31.46±0.37	64.85±0.95	9.30±0.04	3.43±0.14	0.99±0.03	21.44±0.99
Post-digestate (1) Oil	27.09±0.58	60.05±0.36	8.42±0.38	3.21±0.02	2.34±0.11	26.00±0.87

Table 3.3: Bio-oil properties for each feedstock type with a reaction temperature of 325°C, RT=4 min, HR=270°C/min and 6% solids.

Figure3.113.11 3.11 shows the elemental compositions of the initial feedstocks and their corresponding bio-oils. The pre-digestate feedstock had a higher H/C ratio and lower N/C, S/C and O/C ratios than the post-digestate feedstock. These trends make sense considering that anaerobic digestion mainly creates methane and carbon dioxide products. In this case, since digestion decreases the H/C ratio and drastically increases the O/C ratio, a large portion of the gas products are methane rather than carbon dioxide. The composition of the bio-oil products parallel to their respective initial feedstocks. The pre-digestate begins with the lower heteroatom content, and its derived bio-oil does as well, resulting in a higher HHV. The pre-digestate sludge is therefore preferable when considering the HTL process in isolation. Using the pre-digestate sludge, however, would eliminate methane production during anaerobic digestion. Bond (2015) thoroughly considers the tradeoffs between bio-oil quality and methane production [7]

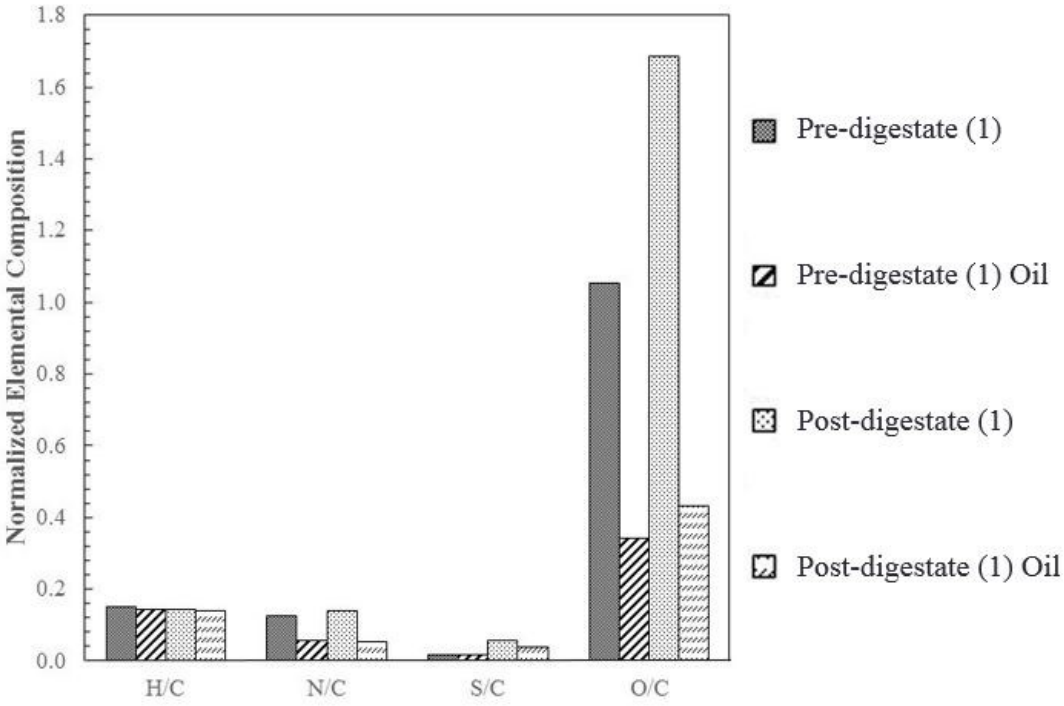

Figure 3.11: Composition of biosolids before and after HTL. The process conditions were 325°C, TR=4 min and HR=270°C/min. The feedstock had 6.2% solids.

3.4 Chapter Conclusions and Recommendations

This chapter presented and experimental study converting pre-digestate sludge and post-digestate biosolids to bio-oil via hydrothermal liquefaction (HTL) in batch reactors. The highest quality oil had a HHV of 31.46±0.37 MJ/kg with a yield of 39.42±1.4%. This was obtained using the pre-digestate feedstock with 6.2% solids when processing at 325°C reaction temperature, a 270°C/min heating rate and 4 minutes of residence time. Moreover, the following trends were observed in the results of parametric experiments:

1. The yield and HHV were not sensitive to changes in residence time from 4 to 25 minutes at a reaction temperature of 325ºC and heating rate of 270ºC/min with 6.2% solids in the feedstock. This indicates that the reactions were complete by 4 minutes.
2. The highest yield was achieved at an intermediate heating rate of 270°C/min at a reaction temperature of 325ºC and residence time of 4 minutes with pre-digestate feedstock at 6.2% solids. However, the HHV was not sensitive to the heating rates from 130°C/min to 508°C/min with any statistical significance for either feedstock. The reaction kinetics specific to proteins, carbohydrates, lipids and fibers may explain how different feedstocks respond to changes in heating rate.
3. The highest yield of 83.5% and lowest HHV of 23.02 MJ/kg were obtained for a 1% solids concentration at a reaction temperature of 325ºC and residence time of 4 minutes with pre-digestate feedstock. With increasing solids concentrations, the yields decreased, but the produced bio-oils had higher HHVs. High amounts of water in the feedstock may increase depolymerization and decomposition of organic matter but inhibit the reformation of long-chain hydrocarbons.

4. The higher heating value (HHV) of pre-digestate was upgraded from 15.50 MJ/kg to 31.02 MJ/kg while that of post-digestate was upgraded from 8.12 MJ/kg to 27.90 MJ/kg through hydrothermal liquefaction. The pre-digestate feedstock resulted in a higher quality bio-oil.

Future work in batch reactor experiments should include the HTL of pre-digestate sludge with a wide range of solids concentrations (1% to above 33%). Higher solids concentrations may result in higher HHVs than reported in this thesis, and testing a wide range may help explain discrepancies with Yin et al. and He et al. [17,19]. Lastly, the effect of heating rate should be further explored by better characterizing several types of biomass and then processing them at the same set of heating rates. This may help describe the complex reaction kinetics associated with different types of organic matter.

Chapter 4: Continuous HTL System Design and Construction

4.1 Introduction

This Chapter presents the design and construction of a continuous HTL system. The goal was to design a fully instrumented experimental system that could be used to assess the effect of the heating rate, set point temperature, residence time and feedstock solids concentration on HTL performance.

4.2 Design Specifications

A summary of the target design specifications is provided in Table 4.1. A heating rate of over 230°C/min was desired because results by Faeth et al. (2013) showed that high heating rates produced much higher bio-oil oil yields when converting algae feedstock in batch [15]. The reaction temperature range of 285°C to 350°C was chosen based on literature that showed these as the bounds for favorable HTL [18]. The residence time above 200°C was desired to range from 1 to 30 minutes. Batch tests by Faeth at high heating rates and by Suzuki and low heating rates both used 0 minutes of residence time at the set point temperature while several other papers, such as Vardon, used longer times up to 30 minutes [1,2,15]. The range in feedstock solids concentration was targeted to be 1% to 6% for the sake of demonstrating trends. In a scaled up system that would be used in the industry, all orifices, valves and pipes would be much larger, which would actually make it easier to pump a slurry with a higher solids concentration. A feedstock flow rate of greater than 5 mL/min was required so that sufficient bio-oil could be obtained in one day of testing for simulated distillation, heat of combustion which required 30mL and 50mL of product, respectively. At 5 mL/min, it would take 12.5 hours to produce 80mL of bio-oil assuming a 40% yield on pre-digestate (1) from Chapter 3. An upper bound of 20 mL/min was chosen based on the piping length and is further explained in Section 4.2.2.

Specification	Quantification	Justification
Pressure	200 bar (3200 psi)	Required to keep water subcritical
Heating Rate	>230°C/min	Findings by Faeth et al. suggest high heating rates result in higher yields
Reaction Temperature	285°C to 370°C	Range of possible conversion temperatures for HTL
Residence Time	1 to 30 minutes	Several papers have differing results across this wide range of residence times
Solids Concentration	0 to 6 wt.%	Range of feedstocks available from Hornsby Bend
Flow Rate	>5 mL/min	Required to create sufficient bio-oil

Table 4.1: Continuous system design specifications.

4.2 CONCEPTUAL DESIGN

Figure 4.1 shows the basic conceptual design created to illustrate the major design decisions. The major processes that the biomass slurry must undergo are: pressurization, heat up, residence time, cool down, depressurization, and oil separation. The following sections show how specific equipment was chosen to complete each of these processes.

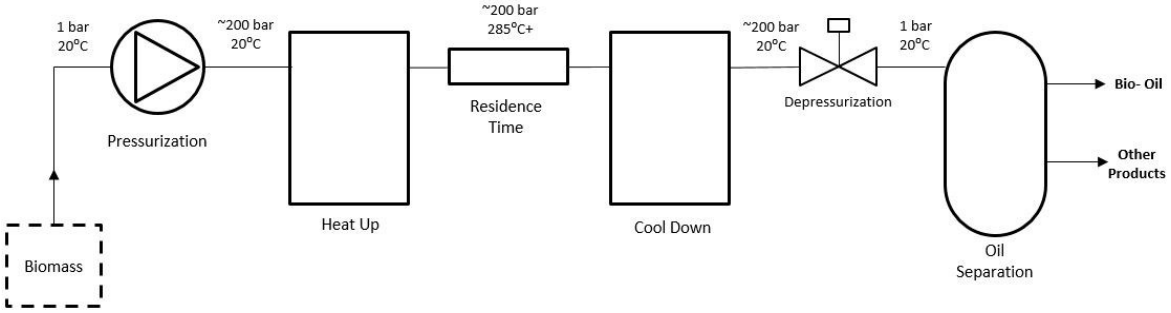

Figure 4.1: Basic conceptual design for the continuous system.

4.2.1 Pressurization

The pump was required to reach sufficient pressure for HTL, have the ability to process a viscous slurry with solid particles and operate at a sufficient flow rate to produce

enough bio-oil for analysis. To keep water subcritical at the maximum design point of 370°C, a pressure of 220 bar was necessary.

Several types of pumps were considered, with the main issue being the ability to pump liquids with solid particles. High performance liquid chromatography pumps were considered, as several of them were able to pump viscous and volatile fluids at the necessary pressures and flow rates. After feedback from HPLC pump engineers and technicians, it was determined that the solid particulates in the slurry would present too great of a risk of damaging the pump.

Homogenization pumps, such as the pump used by Jazwari et al., were considered, but they were generally made to pump much higher flow rates (~30-50,000 L/h) than desirable for a laboratory-scale system and were too expensive. The pump used by Jazwari et al. (GEA Niro Soavi Ariete NS3006) pumped a flow rate of 50-1000 L/h and cost ~$80,000.

Syringe pumps were chosen as the appropriate pump type because they had the ability to pump slurries with solid particles and were made to process low flow rates at pressures. Two syringe pumps can be linked and run continuously so that one syringe is pumping with the other is refilling. The syringe pumps used by Elliot et al. (Model 500D; Teledyne ISCO) were made with the specific purpose of handling slurries and pastes and had the advantage of already being proven to work for the similar application of processing algae based slurry [11].

4.2.2 Heat-Up Process

The two major options for heating up the biomass used in previous literature were a stirred vessel or high pressure piping that ran through a heating source. High pressure

piping was chosen because it allowed the heating profile of the biomass slurry to be more easily controlled and measured while also being the simpler and cheaper option.

The first heating component considered was a fluidized heating bath, which was used by Jazwari et al. A fluidized heating bath was preferred because its temperature could be very precisely controlled, it was relatively inexpensive and it could also be used for batch experiments. The heat transfer into the high pressure piping system was modelled in order to determine if a fluidized sand bath was a feasible option and to select a bath of the appropriate size and power. The energy balance for a pipe subject to a constant heat flux boundary conditions yields [31],

$$\dot{m}c_p dT_m = q' dx \tag{1}$$

where T_m is the mean fluid temperature, q' is the heat flux per unit length, x is the distance downstream, $\dot{m}$ is the mass flow rate, and c_p is the specific heat of the fluid. In this case, the heat flux q' depends on the total effective resistance of the pipe, which includes the external convection from the heating bath, the conduction through the steel piping and the internal convection of the flowing biomass slurry. The effective resistance per unit length is given as,

$$R_{l,eff} = \frac{1}{2\pi r_o h_b} + \frac{\ln(r_o/r_i)}{2\pi k_s} + \frac{1}{2\pi r_o h_i} \tag{2}$$

where $R_{l,eff}$ is the effective resistance of the system per unit length, r_o is the outer radius, r_i is the inner radius, k_s is the conductivity of steel, h_b is the convection coefficient for the heating bath and h_i is the convection coefficient for the internal flow. The heat transfer coefficient for fluidized sand baths is subject to change based on air flow rate and sand properties, but can be approximated as 300W/(m^2·K) [32]. The convection coefficient for

the internal flow h_i was approximated from a Nusselt number correlation for a fully developed flow in a pipe as,

$$Nu = \frac{h_i D_i}{k_f} = 3.66 \tag{3}$$

where Nu is the Nusselt number, k_f is the thermal conductivity of the fluid and D_i is the internal pipe diameter. Thus, the internal convection coefficient can be easily solved for using Equation (3). All variables that make up the equation for $R_{l,eff}$ are then known, and the heat rate per unit length can be written as,

$$q' = \frac{T_b - T_m}{R_{l,eff}} \tag{4}$$

Substituting Equation (4) in Equation (5) enables us to determine the mean temperature of the flow at any point along the length of the tube as,

$$T_m(x) = T_b + (T_0 - T_b)e^{-\frac{x}{R_{l,eff}\dot{m}c_p}} \tag{5}$$

where T_0 is the initial temperature of the biomass slurry when it enters the piping. This equation was used to generate a slurry temperature profile with respect to either the length of the pipe or time. This curve was then used to determine the heating rate and the length of pipe required to reach the desired fluid temperature. The heating rate was calculated in the approximately linear regime between 100-250°C and was desired to match and exceed the heating rate of 230°C/min achieved in batch experiments by Faeth et al [15]. The length was calculated with 300°C as the nominal desired fluid temperature and a target length on the order of magnitude of 10-100cm simply so that the pipe would easily fit in a laboratory setting. The total heat required by the sand bath was then calculated by summing the heat flow along the pipe with the integral in equation (6).

$$\dot{Q}_{tot} = \int_{x=0}^{x=L} \frac{(T_h - T_m(x))}{R_{l,eff}} dx \tag{6}$$

To carry out the integration, Equation (5) was substituted for $T_m(x)$. The definite integral was computed numerically using MATLAB. This heating requirement was calculated in

order to size the heater. The results of this analysis are shown in Table 4.2. The variable inputs were the pipe diameter, heating bath temperature and flow rate. The max heating bath temperature was chosen based on specifications for Techne brand fluidized sand baths, and the pipe diameters were chosen because they generated near-desired heating rates and Swagelok did not offer the full range of products in any sizes between ¼" and ½".

Inputs			Outputs		
Pipe Outer Diameter (in)	Heating Bath Temperature (°C)	Flow Rate (mL/min)	Heating Rate (°C/min)	Power Required (W)	Pipe Length (cm)
1/4	600	5	1235	95	9.4
		20	1235	384	37.8
	350	5	480	95	37.2
		20	480	384	109
1/2	600	5	220	95	7.5
		20	220	384	30.1
	350	5	86	95	21.7
		20	86	384	86.8

Table 4.2: Results of thermal model simulations. All cases considered heating rate to be from 100 to 250°C, h_{bath}=300W/m2K and the length required to be in order for the fluid to reach 300°C.

In the thermal model, the lowest flow rate considered was 5 mL/min so that sufficient bio-oil would be produced. Higher flow rates were tested in the model and resulted in an increase in required pipe length. At 20 mL/min, the pipe length just exceeded the target length of 1 meter, so it was considered the upper bound on flow rate. The thermal model simulation results showed that ¼" pipe could be used with Techne's SBS-4 fluidized sand bath to achieve the required heating rate. The SBS-4 had a nominal heater power of 1500W which met the modeled power requirement with a safety factor of over three. The

SBS-4 had a working volume of 17.8cm diameter and 14.0cm depth, which was enough to fit the required pipe lengths generated in the model.

4.2.3 Residence Time at the Reaction Temperature

Because the sand bath was at a high temperature to induce fast heating rates, the slurry needed to be held at its reaction temperature outside of the sand bath. Additional piping outside of the sand bath was used to keep the slurry at its reaction temperature. The three main parameters to consider were the length of the extra piping, the amount of insulation, and amount of additional heating. The required length of the piping was easily determined with the flow rate and residence time requirements. The required residence time of 30 minutes could be achieved with 1.84 meters of piping at a flow rate of 5 mL/min. In order to keep the same heating rate and temperature parameters while easily varying residence time, the system was designed to have three different piping length options for the slurry to flow through. The system would be designed so that any of the three options could be used during a given test run by using valves or slightly adjusting the setup. Table 4.3 shows three piping length options that allow for the required residence time variation.

Flow Rate (mL/min)	Pipe Length 1 (cm)	Residence Time 1 (min)	Pipe Length 2 (cm)	Residence Time 2 (min)	Pipe Length 3 (cm)	Residence Time 3 (min)
5	184	30.1	61	10.0	6	1.0
20	184	7.5	61	2.5	6	0.2

Table 4.3: Residence times achieved with given flow rate and pipe length parameters.

To determine if an additional heat source was necessary, equations (2) and (5) were modified. In the holding time situation, the equation to find $R_{l,eff}$ was changed to reflect the fact that the piping was exposed to the ambient atmosphere rather than the heating bath

and to incorporate the possibility of using additional insulation. The new expression for $R_{l,eff}$ can be written as,

$$R_{l,eff} = \frac{1}{2\pi r_{ins} h_{atm}} + \frac{\ln(r_{ins}/r_o)}{2\pi k_{ins}} + \frac{\ln(r_o/r_i)}{2\pi k_s} + \frac{1}{2\pi r_o h_i} \quad (7)$$

where r_{ins} is the outer radius of added insulation, h_{atm} is the atmospheric convection coefficient and k_{ins} is the heat transfer coefficient for the insulation. The mean temperature equation was modified to use the ambient temperature rather than the bath temperature,

$$T_m(x) = T_{atm} + (T_h - T_{atm}) e^{-\frac{x}{R_{l,eff}\dot{m}c_p}} \quad (8)$$

where T_{atm} is the ambient temperature and T_h is the initial temperature of the slurry when it leaves the heating bath. This analysis immediately showed that insulation alone would not be sufficient to keep the slurry near its set point temperature for a sufficient residence time. The appropriate high-temperature insulation was determined to have $k_{ins} = 0.33 W/(m \cdot K)$ and to be easily obtainable with a diameter of up to 3". With these specifications, however, the slurry would cool from 300°C to 295°C within 0.7 minutes. Even with an impractical insulation diameter of 1 foot, the slurry would cool down 5°C within 1.3 minutes.

Thus, in order to keep the slurry near its reaction temperature for specified residence times of up to 30 minutes, supplementary heating was required. To decide on the heating requirement, Equation (4) was modified to include supplementary heating q'_{sup} (9). To keep the fluid temperature constant, the heat flux should be zero.

$$q' = \frac{T_{atm} - T_m}{R_{l,eff}} + q'_{sup} = 0 \ \therefore \ \frac{T_m - T_{atm}}{R_{l,eff}} = q'_{sup} \quad (9)$$

With no added insulation and T_{atm}=25°C, equation (9) showed that 260W/m of supplementary heating would be required to keep the slurry at the maximum reaction temperature of 350°C. Based on the max pipe length of 184cm, 480W of total heating would be required to provide 260W/m. Several flexible heaters that could wrap around the

pipe were considered. A heating cord was selected that had high enough power output, high enough exposure temperature and small enough wraparound diameter. Two cords (Model HTC-120; Omega Engineering, Bridgeport, NJ) that each output 260W were selected. A temperature controller (Model CN743; Omega Engineering) was also selected to regulate the hold time temperature.

4.2.4 Cool-Down Process

After the slurry was held at the reaction temperature for the desired residence time, it needed to be cooled to atmospheric temperature before depressurization in order to remain in the liquid state throughout. A piping system that ran through an isotemperature water bath was considered because it was a simple solution that utilized equipment already in the lab. Cooling rate was a fixed variable, so the exact rate was not important. It was only important that the rate be consistent and the bath have the sufficient power to bring the slurry down to the atmospheric temperature. The system was modeled using the same methodology as for the heat up process using modified versions of Equations (2), (5) and (6) to solve the temperature profile and total energy required. Equation (2) only differed in that a new external convection coefficient h_b needed to be calculated that was specific to the cooling bath. This was calculated using the Nusselt number correlation for flow over a cylinder,

$$Nu_D = 0.683 Re_D^{0.466} Pr^{1/3} \; for \; 40 < Re < 4{,}000, Pr \geq 0.7 \qquad (10)$$

where Nu_D is the Nusselt number, Re_D is the Reynolds number and Pr is the Prandalt number. In order to calculate the Reynolds number, the external velocity was estimated using the flow rate and area of a cooling bath already used in the lab (Model 1013P; Thermo Fischer Scientific, Waltham, MA). In equations (5) and (6), the initial temperature T_0 was

set as 350°C, and the bath temperature was set to 20°C. The inputs and outputs for this analysis are given in Table 4.4.

Inputs			Outputs		
Pipe Diameter (in)	Cooling Bath Temperature (°C)	Flow Rate (mL/min)	Cooling Rate (°C/min)	Cooling Required (W)	Pipe Length (cm)
1/4	20	5	75	114	49
		20	75	454	194

Table 4.4: Cooling rate and required power.

The cooling bath at the lab had a cooling capacity of 350W at 20°C, which meant that it would be sufficient for a 5mL/min flow rate but not at 20mL/min flow rate. To achieve full cooling at the target range of flow rates, a different circulating bath with a greater cooling capacity of 500W was chosen (Model SC100-A25B; Thermo Fischer Scientific); however, it was not purchased since the in-house bath allowed a sufficient flow rate range to begin testing.

4.2.5 Depressurization

A pressure control valve was required to keep the flow at high pressure upstream and convert it to a low pressure for product collection downstream. In valve selection, the flow coefficient C_v is commonly used to relate the flow rate and pressure drop. The valve coefficient is calculated as [33],

$$C_v = Q(GPM) \cdot \sqrt{\frac{\gamma}{PD\ (psi)}} \tag{11}$$

where γ is the specific gravity and PD is the pressure drop across the valve. Based on the design flow rate range of the system, the C_v needed to be adjustable from $2.3x10^{-5}$ to $9.3x10^{-5}$. Because of the low flow and high pressure drop required of a laboratory scale

HTL system, this C_v range is unusually low. Valves made specifically for laboratory scale systems were found at Badger Meter, which supplied the valve for the system by Jazwari et al. [10]. Based on the required C_v range, a needle valve was selected that had a C_v range from $1.8x10^{-5}$ to $2.7x10^{-4}$ was chosen (Model 1001GCN36SVOSP06ST, Badger Meter, Madison, WI). The valve orifice diameter (and thus C_v) was controlled by air pressure, which could be manually adjusted.

4.2.6 Oil Separation

After depressurization, the product stream needed to be separated into its gas, oil, aqueous and solids phases. An enclosed vessel with a gas outlet at the top and liquids and solids outlet at the bottom could easily separate the gas. The remaining solids and liquids mix could be separated using the same chemical methods used during batch experiments.

4.2.7 Measurement Instrumentation

In order to track the desired parameters of heating rate, set point temperature, cooling rate and pressure, several thermocouples and a pressure sensor were necessary. For the heating and cooling sections, two or more thermocouples were required in order to estimate the heating and cooling curves. A thermocouple was also required to track the temperature fluctuations as the slurry was held at its reaction temperature. All thermocouples were ¼" type K thermocouples (101-K-U-C-2-C; Ultra Electronics) swaged into piping tee joints. A pressure transducer was required before the needle valve to ensure subcritical conditions throughout the system. The transducer chosen (PX44E0-1KGI; Omega Engineering) was specifically made for measurement of viscous slurries.

4.3 Finalized Design and Construction

All equipment was selected based on heat transfer and energy requirements, but the geometry of the system had not yet been thoroughly considered. The system was created

on SolidWorks in order finalize the geometry and bill of materials. Figure 4.2 shows the initial SolidWorks rendering of the entire system.

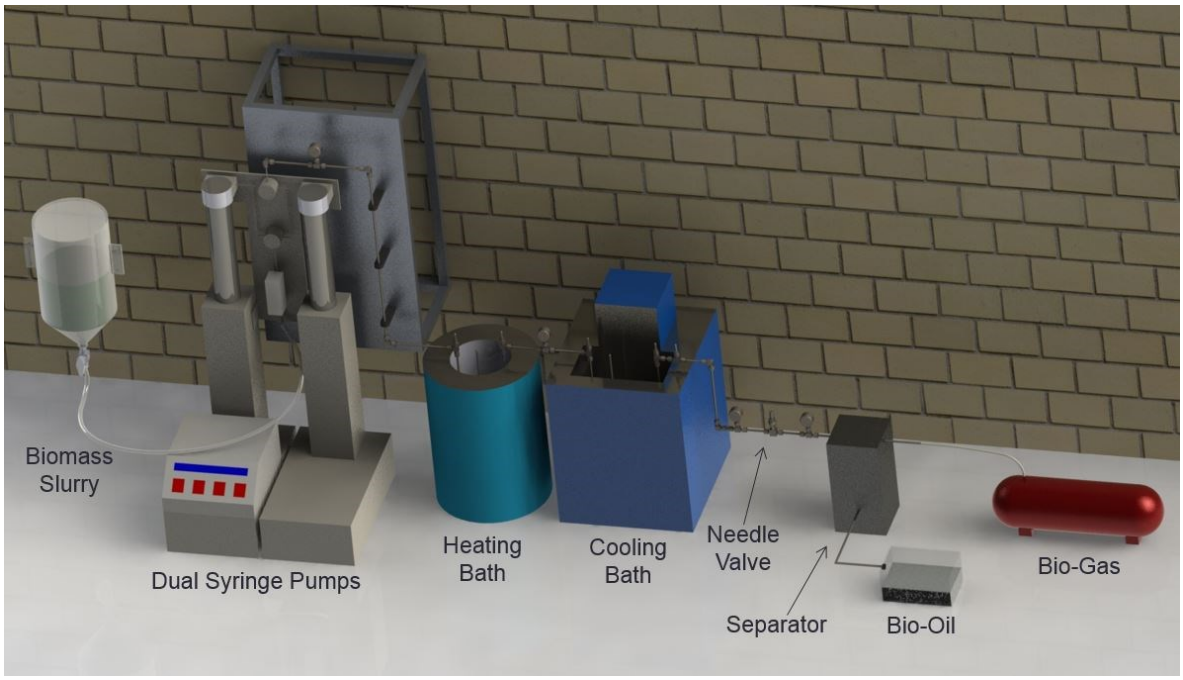

Figure 4.2: Continuous system design.

Two main modifications were made to this system during the construction process. First, the residence time module, pictured in Figure 4.3, was created. Coiled piping was wrapped in the heating wire, surrounded by high-temperature insulation (FAAE001; Bay Fabrication Company; Green Bay, WI) and enclosed in a box made of aluminum sheet. Openings in the aluminum sheet allowed the controller to connect to the heating wires and thermocouple. The assembly was held in position by steel struts.

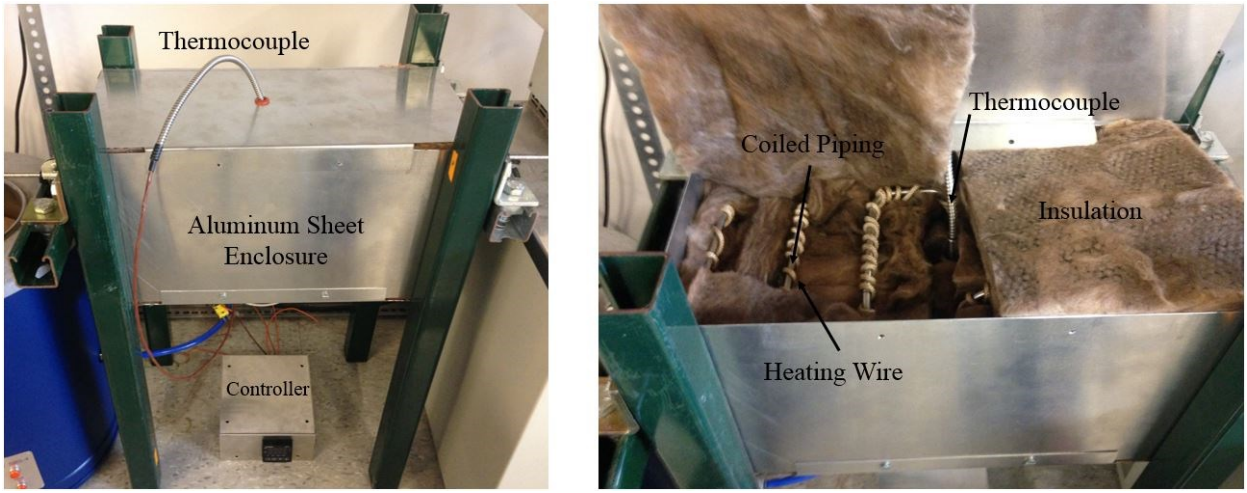

Figure 4.3: The residence time module. (left) The full module assembled as it would be during use, and (right) the interior workings of the module.

The second modification was the construction of a base to hold the pressure transducer, the needle valve and a flushing valve. The base is shown in Figure 4.4. Steel struts and aluminum sheet were used to secure each element.

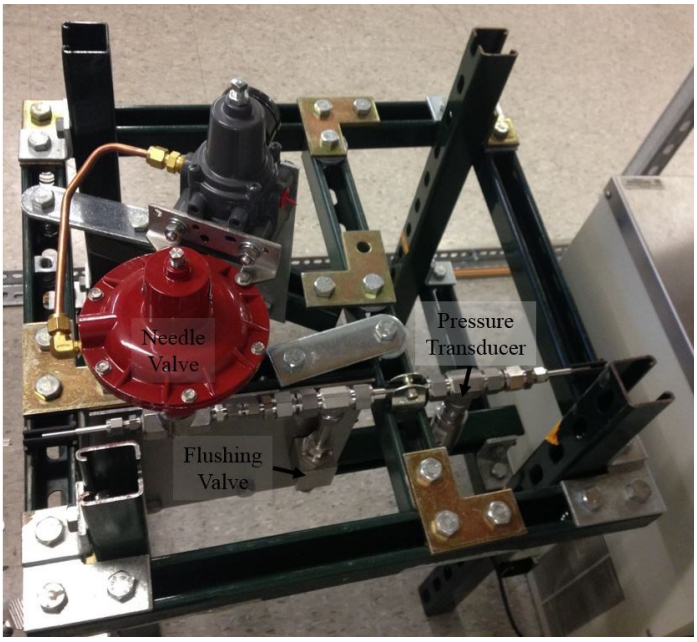

Figure 4.4: Base for the pressure transducer, needle valve and flushing valve.

The complete system is pictured in Figure 4.5, and a bill of materials is provided in Appendix 1.

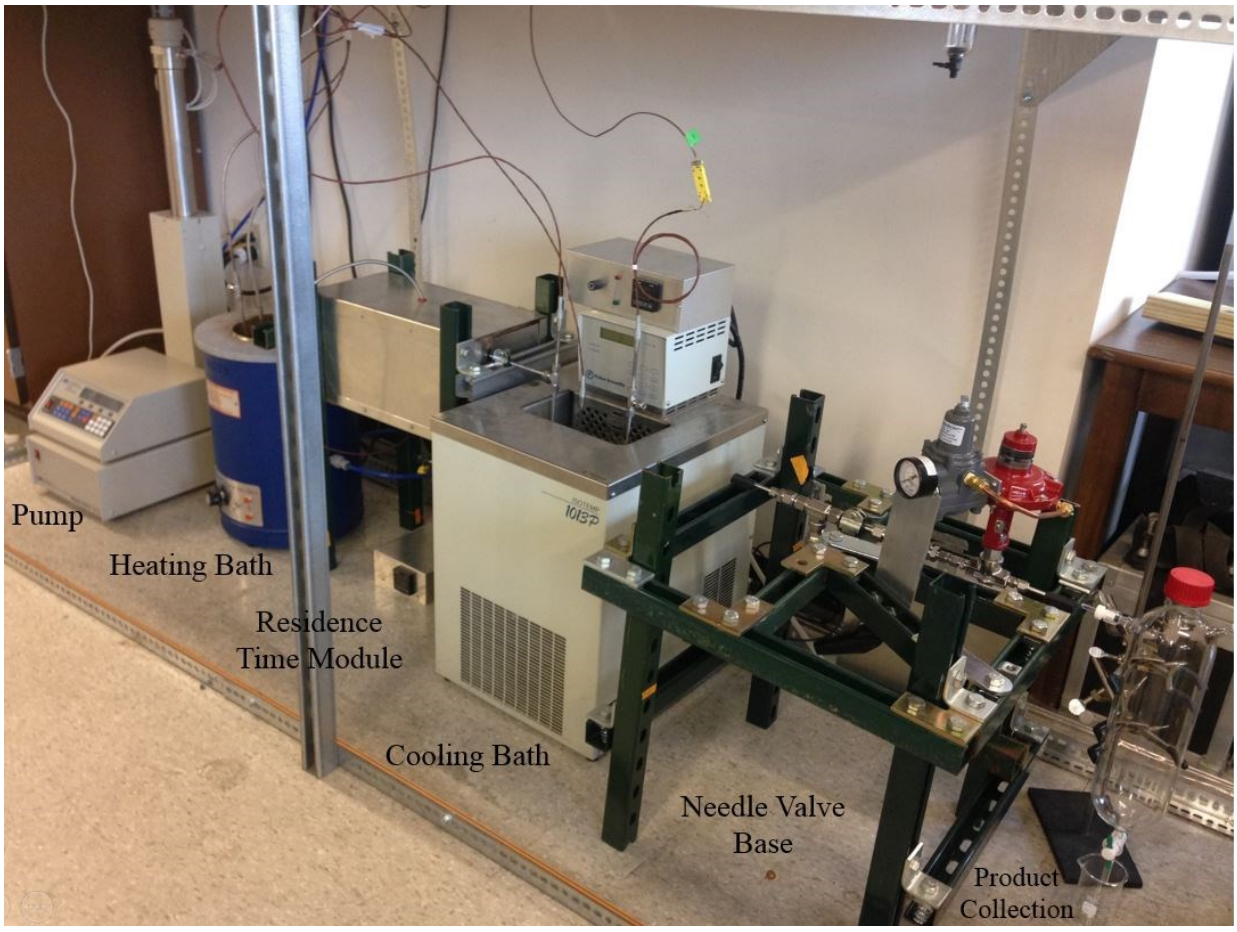

Figure 4.5: Complete continuous system.

4.4 Chapter Conclusions and Recommendations

A continuous system for the hydrothermal liquefaction of municipal sludge and biosolids was designed and constructed. The system was designed to process 5mL/min to 20mL/min of slurry for the purpose of demonstrating feasibility and conducting testing with a variety of process conditions. The design was based on previous continuous HTL systems and fundamental heat transfer principles.

No experiments were run with the continuous system, so future work should begin with the operation of the continuous system. Future work should also include the verification of bio-oil yield and composition trends related to the heating rate, residence time, feedstock solids percentage and feedstock composition that were demonstrated in Chapter 3 with batch reactors.

Chapter 5: Conclusions and Recommendations

The thesis discussed the hydrothermal liquefaction of municipal sludge and biosolids as both a batch and continuous process. Batch experiments were conducted to explore the effect that process conditions and feedstock conditions had on the resulting bio-oil. The HHV of the bio-oil was unaffected by residence time and heating rate but increased with increasing solids concentration and HHV of the initial biomass. The bio-oil yield was unaffected by residence time but much higher at the lowest solids concentration. The midrange heating rate resulted in the best yield, which may be explained by the complex optimization of reactions that take place at temperatures throughout the HTL process. The highest quality bio-oil had a HHV of 31.46±0.37 MJ/kg with a yield of 39.42±1.4% and occurred at a 270°C/min heating rate, residence time of 4 minutes a solids concentration of 6.2% with the pre-digestate sludge.

Future work concerning batch experiments may include exploring the mechanisms during the heating up process that effect the bio-oil yield and composition. One such experiment could use a forage analysis of several different biomass types to predict the outcome based on the hydrolysis and decomposition tendencies for the biomass's contents. Other work could be to test higher solids concentrations of the pre-digestate sludge to achieve much higher HHVs and to further monitor the trend in the bio-oil yield. This work will be more pertinent once a continuous system is scaled up and is capable of handling slurries with high solids concentrations.

The design of a continuous system for the HTL of municipal sludge and biosolids was also presented in this thesis, however the system has yet to be operated. The obvious

future work for this aspect of the project will be to run the system to show proof-of-concept and to gather data concerning bio-oil yield and composition at various processing conditions.

Appendix 1: Bill of Materials

Pressurization			
Description	QTY	Vendor	Part #
High Pressure Syringe Pump	1	Teledyne ISCO	500D
Heat-Up			
Description	QTY	Vendor	Part #
Fluidized Sand Bath	1	Techne Calibration	SBS-4
Sand Bath Controller	1	Techne Calibration	TC-9D
1/4" dia, 3" length, Type K Thermocouple w/armor	2	Ultra Electronics	101-K-U-C-2-C-003.0-Z036-Y012
1/4" dia, 6" length, Type K Thermocouple w/armor	1	Ultra Electronics	101-K-U-C-2-C-006.0-Z036-Y012
1/4" Stainless Steel Union Tee	2	Swagelok	SS-400-3
1/4" Stainless Steel Union Elbow	2	Swagelok	SS-400-9
1/4" Stainless Steel Tube - 7" Section	2	Swagelok	SS-T4-S-094-20
1/4" Stainless Steel Tube - 3" Section	1	Swagelok	SS-T4-S-094-20
1/4" Stainless Steel Port Connector	1	Swagelok	SS-401-PC
Residence Time			
Description	QTY	Vendor	Part #
Heating Cord	2	Omega Engineering	HTC-120
Controller	1	Omega Engineering	CN742
Custom Aluminum Box - 17" x 8.5" x 8"	1	NA	NA
Custom Aluminum Box - 6" x 6.5" x 3"	1	NA	NA
1/4" dia, 6" length, Type K Thermocouple w/armor	1	Ultra Electronics	101-K-U-C-2-C-006.0-Z036-Y012
1/4" Stainless Steel Tube - 128" Coiled Section	1	Swagelok	SS-T4-S-094-20
1/4" Stainless Steel Union Tee	1	Swagelok	SS-400-3
Standard Steel Strut Channel - 26" Section	4	McMaster-Carr	3310T174
Standard Steel Strut Channel - 14" Section	2	McMaster-Carr	3310T174
90° Strut Channel Connector	4	McMaster-Carr	33125T32
Stud Nut & Bolt for Strut Channel	8	McMaster-Carr	3580T31
1/4" OD Strut-Mount Clamp	2	McMaster-Carr	32625T49
High Temperature Insulation	1	McMaster-Carr	9356K11
Cool Down			
Description	QTY	Vendor	Part #
Cooling Bath	1	Fischer Scientific	1013P
1/4" dia, 3" length, Type K Thermocouple	2	Ultra Electronics	101-K-U-C-2-C-003.0-Z036
1/4" dia, 6" length, Type K Thermocouple	1	Ultra Electronics	101-K-U-C-2-C-006.0-Z036
1/4" Stainless Steel Union Tee	2	Swagelok	SS-400-3
1/4" Stainless Steel Union Elbow	2	Swagelok	SS-400-9

1/4" Stainless Steel Tube - 8" Section	2	Swagelok	SS-T4-S-094-20
1/4" Stainless Steel Tube - 4" Section	1	Swagelok	SS-T4-S-094-20
1/4" Stainless Steel Port Connector	1	Swagelok	SS-401-PC
Depressurization			
Description	QTY	Vendor	Part #
Pressure Transducer	1	Omega Engineering	PX44E0-1KGI
Ball Valve	1	Swagelok	SS-AFSS8
Needle Valve	1	Badger Meter	1001GCN36SVOSP06ST
Custom Aluminum Needle Valve Support	1	NA	NA
Custom Aluminum Ball Valve Support	1	NA	NA
1/2" Stainless Steel Female Branch Tee	1	Swagelok	SS-810-3-8TTF
1/2" Stainless Steel Union Tee	1	Swagelok	SS-810-3
1/2" to 1/4" Stainless Steel Reducing Union	2	Swagelok	SS-810-6-4
1/4" Tube to MNPT Connector	2	Swagelok	SS-400-1-4
1/4" Stainless Steel Tube - 12" Section	1	Swagelok	SS-T4-S-094-20
1/4" Stainless Steel Tube - 6" Section	1	Swagelok	SS-T4-S-094-20
1/4" Stainless Steel Tube - 3" Section	2	Swagelok	ARTHR-5051
1/4" Stainless Steel Port Connector	1	Swagelok	SS-401-PC
1/2" Stainless Steel Port Connector	2	Swagelok	SS-811-PC
1/4" OD Strut-Mount Clamp	2	McMaster-Carr	32625T49
1/2" OD Strut-Mount Clamp	2	McMaster-Carr	32625T52
Standard Steel Strut Channel - 25" Section	4	McMaster-Carr	3310T174
Standard Steel Strut Channel - 21" Section	3	McMaster-Carr	3310T174
Standard Steel Strut Channel - 17" Section	5	McMaster-Carr	3310T174
Standard Steel Strut Channel - 10" Section	1	McMaster-Carr	3310T174
90° Strut Channel Connector	10	McMaster-Carr	33125T32
Corner Strut Channel Connector	8	McMaster-Carr	33125T136
Straight Strut Channel Connector	2	McMaster-Carr	33125T129
Stud Nut & Bolt for Strut Channel	46	McMaster-Carr	3580T31
Separation			
Description	QTY	Vendor	Part #
Custom Glass Vessel	1	NA	NA
3/8" ID Flexible Polyethylene Tubing	1	McMaster-Carr	9336T2

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